THE CONSTITUTION OF LIQUID SLAGS

THESIS

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by

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PART 1.

INTRODUCTION.

By far the greatest amount of work which has been carried out on liquid slags has been in the field of slag metal equilibrium studies. From these a knowledge of the activity of each component is obtained. However increasing attention is now being paid to the actual constitution of the liquid slag by making measurements of the physical properties of the liquid material. In this way some idea of the spatial arrangement of the atoms in the slag melt can be obtained and correlated with the known thermodynamic properties of the melt.

It is now generally agreed that the liquid state, at temperatures not far removed from the melting point, is structurally similar to the crystalline state but lacks the long range order characteristic of a crystal. Only at temperatures well above the melting point and nearing the critical temperature does a liquid become "gas like" in behaviour and only then should it be regarded in relation to the vapour state. The similarity between solid and liquid is indicated, as pointed out by Frenkel(1), by the small increase in volume (10%) on melting and also by the fact that the latent heat of fusion in general is a small fraction of the latent heat of vaporisation. This latter fact indicates that the cohesive forces between molecules in the liquid near the melting temperature are not very different from those existing in the crystal.

This approach to the constitution of the liquid from the resemblance to the crystalline state is particularly appropriate to silicate slags since reliable measurements on these liquids can only be made for a comparatively short range of temperature above the melting point. Here the cohesive forces of the liquid are the bonds of attraction between oxygen anions and silicon cations and between oxygen anions and other metallic cations.

In the crystalline state, the kinetic motion of the atoms is severely restricted to oscillations about a fixed equilibrium position in a geometrically regular structure. On passing to the liquid state, this restriction is greatly reduced, and the atoms now oscillate about equilibrium positions which are themselves not fixed. In the vapour state, the kinetic motion of the atoms is fully developed. The extent to which the kinetic motion of the atoms in the liquid is restricted determines the properties of the liquid and is dependent on the nature of the units composing the volume of the liquid material. Thus if the unit of which the crystal is built up, retains its identity in the liquid and vapour states, then the liquid state is of short existence and the material vaporises readily. If, however, the crystalline state is made up of units which are incapable of individual existence then the transition to the vapour state is interupted by a long range of liquid existence, and this

liquid is more complex in behaviour than in the above case.

By measuring therefore to what extent the kinetic motion of the units of the liquid is restricted some idea of the magnitude of the cohesive forces can be obtained, and knowing this, an approach to the constitution of the liquid can be made. Thus the energy required to impart the full kinetic motion of the vapour state can be measured as the energy of vaporisation. Also the energy required to move from one equilibrium position to another within the liquid is available as the energy of activation for viscous flow. Conductivity measurements on ionic liquids give the energy of activation for the movement of certain ions in the liquid under the influence of an applied electric field and surface tension measurements indicate the strength of cohesion within the liquid. All these are indicative of the forces of inter-:action restricting the freedom of the units composing the liquid. For liquid slags, reliable methods of measuring surface tension, viscosity and electrical conductivity have been developed and used in elucidating the nature of the liquid.

E.M.F. measurements can also be made on the liquid slag although here the difficulty is in obtaining a suitable electrode. Similarly work on the diffusion of the ionic species present in the slag is being developed as a further method of attack. Together with the application of X-rays, these methods are the principal means whereby knowledge of the constitution of liquid slags can be obtained. In the

past X-ray work has only been applied to silicate glasses at room temperature but its application to liquid slags at temper-:atures of 1600°C is also possible.

The properties of silicate slags are of great interest from the academic point of view since these slags belong to the ionic class of liquid. Of this class, little information is available. Liquid slags are certainly complex ionic liquids in that several ionic species are present and the properties of the liquids are in large part dominated by the powerful polarising influence of the silicon cation on the oxygen anion. The effect on this by the contrapolarising influence of other cations brings about a change in the pro-:perties of the melt which can be recorded as a change in viscosity, in electrical conductivity or in surface tension.

The present work is concerned with the viscous properties of the slags primarily from a structural point of view. The viscous flow of slags has long been an object of study but it is only in recent years that results have been obtained of sufficient reliability in detail to withstand theoretical interpretation with regard to the flow process and the constitution of the liquid. This has been the aim of the present work; to carry out viscosity measurements of good reliability and to interpret the results on theoretical grounds, regarding the nature of flow and the constitution of the liquid. Interpretation has been made on the basis of the reaction rate theory of Eyring which, up to date, has proved

the most fruitful method of approach in the study of rate processes. It has found general application in the study of liquid slags in the fields of electrical conductivity and diffusion. The present work deals with its application to the viscosity of slags.

P A R T 2.

CONSTITUTION OF LIQUID SLAGS.

As indicated in the previous section, the properties of liquid slags can be successfully considered by assuming a close connection between the atomic arrangement in the liquid and in the crystalline silicates. Results are then explained by inference from the knowledge of the crystalline state and in many cases a successful explanation in a qualitative manner has been so obtained. Evidence in support of the above assumption for these materials is not lacking. Thus as indicated by Richardson(2) the entropy of fusion is small (e.g., $MgO.SiO_2$. ΔS = 8 cals./deg.) and this fact suggests that little structural change occurs in passing from the solid to the liquid condition. This is supported by X-ray work on glasses (B.E.Warren et alia(3)). Glasses can be considered as highly viscous liquids in which the atomic arrangement is similar to that existing in the free flowing material at higher temperatures. From results obtained on vitreous silica Warren has shown that the diffraction pattern is a blurred reproduction of the pattern for crystalline silica. That is, the average values of the Si-Si distances and Si-O distances are in agreement with the fixed value of the crystalline material. At high temperatures these distances will alter due to thermal expansion but the inference of similar atomic arrangement in the liquid to that in the solid is justified. The liquid does, of course, lack the long range order characteristic of the crystalline

state. Results from viscosity, surface tension and electrical conductivity all indicate that these liquids have a high degree of strong structural bonding.

The starting material in the consideration of these slag structures is the oxide of silicon SiO_2, which has been shown by Bragg(4) to consist of a three dimensional network of Si^{4+} ions and O^{2-} ions in which the silicon ion is surrounded tetrahedrally by four oxygen ions each at a distance of 1.6Å from the central silicon ion. The corners of each tetrahedron are shared with other tetrahedra such that each oxygen ion is bonded to two silicon ions and the structure builds up infinitely in three dimensions. The term SiO_2 molecule thus becomes meaningless since two oxygen atoms and one silicon atom cannot exist together as a single entity. Silica may therefore be referred to as a polymerised material since continuous directional bonding exists between all the constituent ions of the substance. Why silica should exist in such a form is due, as pointed out by Weyl(5) to the strong potential field of the Si^{4+} ion. To satisfy its valency the Si^{4+} ion need only associate itself with two O^{2-} ions. In such an arrangement however the potential field of the strong Si^{4+} ion is insufficiently screened by the negative oxygen ions and large repulsive forces would be set up when two such units approached each other. Minimum free energy of the system is therefore only achieved when the potential field of the strong polarising cation is sufficiently screened. This is brought about by polymer-

:isation whereby the Si^{4+} ion by virtue of its small ionic radius surrounds itself with 4 O^{2-} ions in the tetrahedral arrangement as described. Silica therefore has a very high melting point and negligible vapour pressure. It may be contrasted with SiS_2 which can be sublimed easily since the strong Si^{4+} ion is effectively screened by the highly polarisable S^{2-} ions. This allows close approach of two cations without marked repulsion.

Similar considerations apply to other cations. However the Si^{4+} ion is one of the strongest ions due to its high charge and small size. Thus ions of equal charge but larger size could not adopt the tetrahedral arrangement of SiO_2 but rather take up arrangements suited to their ionic size. The majority of slag forming oxides, e.g., CaO, MgO, MnO have a NaCl type structure in which each cation is surrounded octahedrally by 6 O^{2-} ions in an infinite three dimensional arrangement. The strong directional bonding characteristic of SiO_2 is however absent because the ions are weaker and have higher coordination number, although here again the concept of one molecule of CaO, MnO, MgO is meaningless. The minimum coordination number of a cation is determined by its size but it may take up coordination numbers greater than this depending on its ionic environment. Thus ions have been observed to show varying coordination numbers.

Ion	Co.Nos.	Ion	Co.Nos.
Na^{+}	6,8	Fe^{++}	4,6,8
Ca^{++}	6,7,8	Mg^{++}	4,6,8
Mn^{++}	4,6,8	Fe^{+++}	4,6
		Al^{+++}	4,5,6

Each cation will surround itself with as many oxygen ions as is necessary to screen its potential field effect-:ively and this will be determined by the polarisability of the oxygen ions available. This in turn depends on the strength of the other cations present in the system. It can be seen that an ion needs to coordinate with more ions of low polarisability than of high polarisability in order to achieve minimum energy. The bond strength of any ion with oxygen will therefore change from one oxide system to another as the polarisability of the oxygen ions change. The bond strength of any ion with oxygen is only unique when the two ions are isolated. In such a case the bonding strength is greater than the coulombic attraction of two spheres of given charge due to the polarisability of the anion.

Even silicon can be forced to take up a coordination number greater than four where it is in the presence of an ion stronger than itself. This is so silicyl phosphate where the oxygen ions are under the influence of the strong P^{5+} ion.(5).

It can be seen therefore that an understanding of the silicate structures can only be arrived at by considering the effect of various cations in the oxygen anions. Addition of one oxide to a slag composition can only be considered with reference to the cations already present in the system. This is well illustrated by the changes in activity of one component with change in composition. In the consideration of slag structures the interest lies in the addition of basic oxide of relatively weak cationic strength to the strong silicate network. The metallic cations can be divided roughly into three classes depending on their ionic strengths (Stanworth(6)). The ionic strength is a function of the charge and size of the ion. Ions of high strength form strong directional covalent bonds with oxygen. These are the glass formers such as Si^{4+}, P^{5+}, B^{3+} Ge^{4+} Ions of lower strength due to larger size or smaller charge show partial tendency to form glasses depending on the presence of other ions. Thus the Al^{3+} ion will not of itself form a glass but in the presence of a small amount of Si^{4+} ions it can do so. This is illustrated in the experiments of Stanworth(6) with calcium aluminates which formed glasses only on the addition of a small percentage of silica. This intermediate class also includes Sn^{2+}, Ti^{4+}, Zr^{3+}.

A third class consists of ions of low strength - Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+} which show no tendency to take part in the four fold coordinated network. These classes are not rigidly divided however and anomalies occur with certain ions. Thus Mg^{2+} and Be^{2+} of normal coordination 6 appear in special cases to adopt coordination 4 and take part in network formation. Their tendency to do this will depend on the composition of the melt. Anomalous effects are also observed in the case of heavy ions such as lead Pb^{2+}. This has an (18+2) electron outer shell and this makes the ion readily polarisable. As a result glasses can be obtained in the Pbo-SiO_2 system up to 75 mol.% Pbo. Stanworth (6). This can only be explained by the polarised Pb^{2+} ions acting as bridges between SiO_2^{4-} tetrahedra to give a continuous structure.

The addition of basic oxide to silica involves a gradual change from a three dimensional and largely covalent network to a six fold coordinated and largely ionic structure. Bragg(4) has shown how the variation in crystalline structure takes place across a binary system by a progressive breaking down of the silicate network as oxygen is added. The addition of metal oxide introduces extra oxygen ions which can only be used up by rupture of the network. Singly bonded oxygens (to Si^{4+}) are formed which become coordinated to the added metal ion and at certain O/Si ratios definite types of silicate structural units seem to persist.

Bragg has given these as follows

O/Si Ratio	Structural Unit.
2/1 (SiO_2)	Infinite 3 dimensional network.
2.5/1 ($MO.2SiO_2$)	Infinite 2 dimensional sheets joined by metal ions. $(Si_2O_5)^{2n-}_n$
3/1 ($MO.SiO_2$)	Infinite chains or rings. $(SiO_3)^{2n-}_n$ or $(Si_4O_{11})^{6n-}_n$
4/1 ($2MO.SiO_2$)	Discrete tetrahedra $(SiO_4)^{4-}$

All basic oxide - silica systems do not show a complete range of compounds due to an immiscibility gap which exists in certain systems at the silica rich end. The extent of this gap increases with increase in ionic strength being a maximum for Fe^{2+} and Mg^{2+} and a minimum for Sr^{2+} . Ions of lower strength than Sr^{2+} only show a tendency to immiscibility and this tendency decreases with ionic strength. As pointed out by Richardson(2) and by Warren and Pincus(7) the existence of this gap is due to the conflicting interests of the added metal ion and the Si^{4+} ion with regard to oxygen. Minimum free energy of the system is achieved for minimum energy and maximum entropy contributions of the added oxide. The latter is effected by complete mixing, i.e., solution of the oxide, while the former is achieved by each ion satisfying its coordination requirements so that the potential field of the ion is screened effectively.

The Si^{4+} ion is always ready to take up oxygen ions of high polarisability and so the addition of a small percentage of a weakly bonded oxide such as Na_2O readily breaks the network and the Na_2O enters solution. At the other extreme the addition of a small amount of a strongly bonded oxide such as MgO leads to the separation of two phases, one of which is almost pure silica. In this case the small Mg^{2+} ion cannot exist in coordination with two oxygens only without a large increase in energy of the system taking place and lacking a compensating increase in entropy. This latter can only be achieved at higher concentrations of basic oxide. Immiscibility therefore occurs and the extent of this would seem to be a function of the cation attraction for oxygen. As pointed out by Bockris et alia(8) the order of increasing tendency to immiscibility and the order of increasing immiscibility is in line with the calculated ionic strengths of the cations with the exception of Fe^{2+}. Here the anomaly may be due to the presence of a small quantity of Fe^{3+} ions.

<u>Increasing Ionic Strength.</u>

K^{+} Na^{+} Li^{+} Ba^{2+} Sr^{2+} Ca^{2+} Mn^{2+} Fe^{2+} Mg^{2+}

<u>Increasing Immiscibility.</u>

K^{+} Na^{+} Li^{+} Ba^{2+} Sr^{2+} Ca^{2+} Mn^{2+} Mg^{2+} Fe^{2+}

The presence of the immiscibility gap reduces the number of compounds which any one oxide can form with silica. Thus sodium shows a disilicate while with Ca^{2+} and Mg^{2+} the highest SiO_2 compounds are the metasilicates, and with Fe^{2+} there exists only $2FeO.SiO_2$.

With the principles of these silicate structures established an approximate and qualitative idea of the arrangement in the liquid state can be gained from a study of the work on viscosity, surface tension, conductivity and X-rays not only on the liquid silicates but also on glasses. Warren and Biscoe(9) reported X-ray work on a soda-silica glass in which they established the Si-Si, Si-O and Na-O distances. From this they drew conclusions which give rise to the random network theory in which the Na^+ ions are considered to be randomly distributed in insterstices throughout the silicate network. These conclusions however have not gone unchallenged since Hartleif(10) also published similar work on the K_2O-SiO_2 system in which he postulated the existence of a certain degree of order in the glass. As pointed out by Weyl(5) and examined by Dietzel(11) Warren's work does not permit of the establishment of the Na^+-Na^+ distances. The question of their distribution therefore remains unresolved. From qualitative consider-:ations it would seem unlikely that the distribution of cations is completely random since the existence of ordered compounds in the crystalline state is evidence of some

prearranging towards order prior to crystallisation. We may therefore expect that in the liquid state, silicate fragments exist bearing a structural relationship to the components which would crystallise at lower temperatures. At the metasilicate composition chains of $(SiO_3)_m^{2m-}$ could predominate with a fairly high degree of order just above the melting point. Between compound compositions fragments of various types are possible with the cations concentrating in areas of the smallest silicate fragments. At higher temperatures the networks will break up with consequent decrease of order and bonding effect on the ions. Distri-:bution of cations will then become more random. These changes on increase in temperature are reflected in the changes of the properties of the melts such as large reduction in viscosity and increase in conductivity. In this connection the work on surface tension(12) is partic-:ularly valuable in that acid melts show a positive temper-:ature coefficient of surface tension. This is explained by the progressive break up of the network as the temperature rises and hence results in higher values of surface tension. Basic melts showed normal surface tension coefficients.

The work on conductivity of silicate melts by Bockris et alia (13) has proved conclusively that conduction in these systems is ionic and depends in acid melts on movement only of the added cation. Conduction is by move-:ment of the cation through the insterstices of the silicate network. That this is so is indicated by a comparison of

the energies of activation for conduction and for viscous flow. The latter has values three to four times that of the former suggesting that viscous flow, at least in acid melts, is dominated by the presence of large silicate anions while conduction depends on the mobility of the added cation. This mobility of the cation is of course affected by the network. However, results not only on conduction but also on surface tension, viscosity and density of glasses show that these properties are not continuous functions of ionic strength. Anomalies arise with various cations particularly when the power of the added ion to attract oxygen approaches that of silicon. Thus Al^{3+} shows decreased conductivity once a certain concentration has been exceeded, due probably to its entry into the network formation like silicon.

The overall qualitative picture of the melt which arises therefore for contents of $SiO_2 \geqslant 2MO.SiO_2$ is that of an assembly of ions in which fragments of silicate net-:work exist and in which the degree of order is dependent on both temperature and composition. The fragments may be of SiO_2, sheets $(Si_2O_5)^{2-}$, rings $(Si_2O_7)^{6-}$, chains $(SiO_3)^{2-}$, or simple $(SiO_4)^{4-}$ tetrahedra and may change with composition and temperature. At each temperature and composition an equilibrium structure will exist and in the liquid state this equilibrium may be considered a dynamic equilibrium with silicate fragments forming and reforming as the ions move about. That such an equilibrium structure exists is supported by work on glasses. The viscosity work of

Lillie(14) shows this quite clearly.

In the liquid state it would be expected that this equilibrium is achieved very rapidly. This is indicated by the lack of hysteresis effect in viscosity and conductivity in the liquid state. In glasses months and even years may be required before an equilibrium structure is attained. This picture of the melt as given above has been successful in explaining many of the known properties of these liquids and as more results are gained more detail of the picture can be fitted into place. This can only be achieved however by combining the results from measurements of physical properties with the measured thermodynamic properties of the constituents of the slag. The physical property chosen in the present work is viscosity and a consideration of the knowledge gained from this is given in a later section.

THE VISCOUS FLOW OF LIQUIDS.

The viscosity of a liquid may qualitatively be described as the internal resistance of the liquid to flow under the action of an applied force. When the liquid is sheared a velocity gradient is set up between the layers of fluid and in the large majority of liquids, the relationship between the stress and the velocity gradient is proportional. The constant of proportionality is the viscosity coefficient η. The viscosity coefficient of a liquid can then be defined as the force in dynes/cm^2 required to maintain a relative velocity of 1 cm/sec. between two layers of fluid 1 cm. apart (Hatchek)(15). When the force required to maintain this condition is 1 dyne/cm^2 then the liquid has a viscosity of 1 Poise. This is the standard unit of viscosity and viscosity so expressed is known as Dynamic Viscosity. (Dimensions $ML^{-1}T^{-1}$). Kinematic Viscosity (γ) is obtained by taking into account the density of the liquid,

$$\gamma = \eta/\rho.$$

Until a comprehensive solution of the liquid state is available no complete explanation of the mechanism of viscous flow can be obtained. Attempts have been made to consider the viscous flow of liquid in relation to the gaseous state. Thus Andrade(16) evolved an equation for the variation of viscosity with temperature on the basis of momentum transfer between molecules during flow. This is the mechanism used to explain the viscosity of the gases. However, in more

modern views of the liquid state(Frenkel)(1) the problem is approached from the relationship to the solid state and this is certainly more reasonable for silicate liquids in which viscosity measurements are made at temperatures little above the melting point. In general it may be said that the viscous flow of liquids at temperatures nearer the melting temperature than the boiling temperature should be considered with reference to an atomic arrangement more akin to the solid than to the gaseous state.

One of the most successful approaches to the problem of viscous flow (for molecular liquids only) was that of McLeod(17) who considered that the viscosity of the liquid is dependent on two factors. One of these is a character-:istic of the liquid and independent of temperature and the other is a factor involving the free space within the liquid. McLeod derived the relationship

$$\eta x^{A} = B.$$

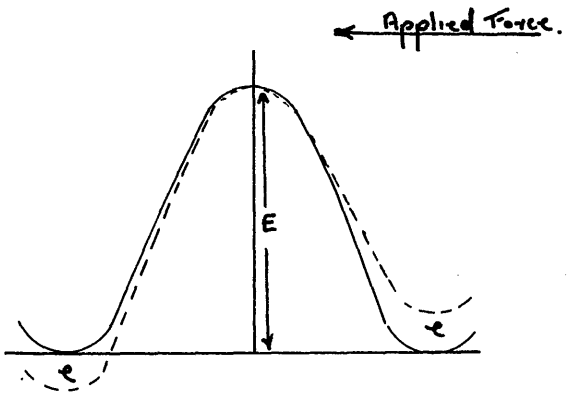
where x is the free space per unit volume and A and B are constants. This was successful for the liquids considered.

All modern attempts at the problem of viscous flow (Bernal)(18), (R.M.Barrer)(19), have been evolved from the approach of Eyring et alia(20) in which viscous flow is treated on the same basis as a chemical reaction. The basic equation is due to S. Arrhenius(21) who expressed success-:fully the rate of a large number of chemical reactions by the equation $k^{*} = A e^{-E/RT}$.

when k* = Rate of Reaction, A = Constant, E = Energy of activation. Working on the basis of this equation, Eyring has evolved the Absolute Reaction Rate Theory for chemical reactions using a statistical mechanical approach. A chemical reaction is considered to take place via the formation of an intermediate activated complex and this requires an activation energy E. The reaction completes itself by decomposition of this complex. Viscous flow may be regarded as a reaction taking place at a definite velocity under given conditions and so the treatment of absolute reaction rate theory is applicable.

When no force is acting on the liquid the molecules may be considered as oscillating about positions of equil-:ibrium. Viscous flow may then be considered to be a movement of units from one equilibrium position to another equilibrium position in the direction of the applied force. This is a unit act of flow. Each equilibrium position is separated from every other by a potential energy barrier and the height of this barrier represents the energy of activation which is required in order that flow may occur. The energy barrier may be considered as symmetrical about the mid point between two positions of equilibrium . At any one temperature a fraction of the total number of molecules will possess sufficient energy to overcome this barrier and molecules will be moving backwards and forwards continually. The application of a force lowers the energy

barrier in the direction of the applied force and hence movement takes place in that direction.



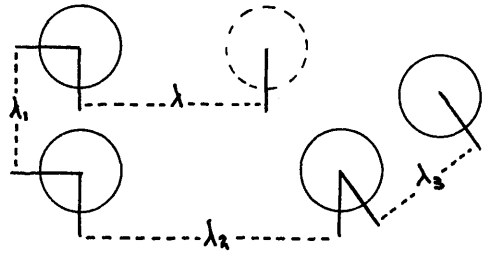
In the consideration of the equation $k^* = Ae^{-E/RT}$ to chemical reactions, the constant A may be regarded as a frequency of collision between reacting molecules. However many chemical reactions have been found to deviate from this equation in that reaction is much slower than would be expected for a given energy of activation E. This indicated a variation in A not explanable by a simple collision hypothesis and Eyring therefore proposed the equation $\eta = A' e^{-\Delta G/RT}$ for the rate of a reaction in which ΔG is the free energy of activation. That is, the controlling factor in a chemical reaction is the free energy of activation and not merely the observed energy of activ-:ation. Since

$$\Delta G = \Delta H - T\Delta S$$

ΔG = Free Energy of Activation ΔH = Heat of Activation ΔS = Entropy of Activation, and $\Delta H = E - RT$ then the pre-exponential term A in the original Arrhenius equation must contain the entropy term $e^{-\Delta S/R}$. This would give a

reason for the failure of a simple collision hypothesis to explain all chemical reactions. Eyring has also shown that the constant $A' = \frac{kT}{h}$ where k = Boltzmann's Constant = 1.4×10^{-16} ergs/degree, and h = Planck's Constant = 6.62×10^{-27} erg.sec. Thus A' is a universal constant independent of the reacting materials.

Similarly in the approach to the viscous flow process Eyring has considered that the controlling factor is the free energy of activation and not the observed energy of activation. Consider a simple molecular liquid in which the moelcules can be regarded as spheres and consider two layers as indicated in the diagram.



Four distances can then be recognised

(1) λ_1 Perpendicular distance between two molecules in adjacent layers.

(2) λ_2 The distance between two molecules in the same layer in the direction of motion.

(3) λ_3 The distance between two molecules in the same layer in a direction perpendicular to the direction of motion.

(4) λ The distance between two equilibrium positions in the same layer in the direction of motion. In such a simple molecular liquid this will probably equal λ_2 .

Working on the basis of this model, Eyring has evolved the equation for viscous flow from the rate equation on the

previous page

$$\eta = \frac{h\lambda_1}{\lambda_2\lambda_3\lambda^2} e^{\Delta G/RT}$$

where h = Planck's Constant, ΔG = Free Energy of Activation for Viscous Flow. On this basis the viscosity is made up of a product of two terms, one of which is concerned with the size of the moving units. The equation may be further resolved

$$\eta = \frac{h\lambda_1}{\lambda_2\lambda_3\lambda^2} e^{\frac{\Delta H - T\Delta S}{RT}} = \frac{h\lambda_1}{\lambda_2\lambda_3\lambda^2} e^{-1} e^{-\Delta S/R} e^{E_\eta/RT}$$

where ΔS = Entropy of Activation and E_η = Observed Energy of Activation. The process of flow therefore on the basis of this equation is controlled by three factors: (1) The size of the moving units, (2) The changes in entropy of the system in attaining the state of activation, (3) The height of the potential energy barrier.

In the simple model of liquid considered above the different λ's may be equated and hence $\frac{\lambda_1}{\lambda_2\lambda_3\lambda^2}$ may be put = N/V where V = Molar Volume and N = Avogardo's No = 6.018×10^{23}. In such a liquid also the changes in entropy will be almost zero so that the equation becomes

$$\eta = \frac{hN}{V} e^{-1} e^{E_\eta/RT}$$

Changes in molar volume with temperature over reasonable ranges of temperature are small and hence

$$\eta = A e^{E_\eta/RT}$$

where A and E_η are constants. This equation had been independently derived by Andrade(16). There is no doubt that it holds well for large classes of liquids and A and

E_η are truly constant over reasonable ranges of temperature. In his treatment of flow, Eyring considers that the system requires greater volume in the activated state and the energy of activation is dependent on the energy required to provide that volume. This immediately suggests the dependence of viscosity on the free volume within the liquid and that this is so is indicated by the large pressure coefficient of viscosity shown by liquids.

This equation $\eta = Ae^{E_\eta/RT}$ may be considered in its application to all classes of liquids and conclusions can then be drawn regarding the differences in behaviour of silicate liquids on the one hand and molecular liquids on the other.

Liquids may be classified, according to the type of forces existing between molecules into two broad classes, polar and non-polar. In the latter class the forces acting between molecules are mainly disperse forces and the molecules can to a great extent act independently as units in themselves. In the polar class, however, interaction takes place between the charged units of the liquid and the units become interdependent. This has a great effect on the properties of these liquids. Silicate melts belong to the ionic group of liquids being composed of metallic cations and oxygen anions. Two attempts have been made, Ward(22) and Harrap & Heymann(23) to apply theories of viscosity to ionic liquids and those attempts have been directed mainly to simple ionic liquids such as the molten

alkali halides. We may expect considerable differences in behaviour between these simple ionic liquids and those involving directional bonding as in silicate melts.

Eyring and co-workers(20) consider that for the process of flow to occur, two distinct energy increments are required, (1) that required to provide room for the molecules to move; (2) that required to move the molecules from one equilibrium position to another. For a large number of liquids of the non-polar class, the second increment is small and apparently invariant over a reasonable range of temperature. These liquids obey well the McLeod relationship between viscosity and free volume. For this class of liquid the dependence of viscosity on free volume is important. The existence of this free volume is one of the characteristics of the liquid state. Eyring considers that the essential difference between a liquid and a solid is due to the introduction of holes to the system. Just as a gas may be considered as molecules moving about in an empty space, so a liquid is to be regarded as holes moving about in matter. While this may be satisfactory as a model for the initial application of the absolute reaction rate theory of viscous flow it implies too strongly the existence of long range order in the liquid. In this respect, the views of Frenkel(1) and Bernal(18) are of more general significance. As Frenkel(1) has pointed out, in crystalline bodies two types of free volume exist. Firstly, there are the

interstices between the constituents of the crystal lattice secondly there are the vacant lattice sites. In the liquid no distinction can be drawn between these two types and Frenkel considers free volume as the space between the spheres of influence of the constituent atoms. This coincides with the earlier views of McLeod.

Bernal also puts a similar interpretation on the liquid state. Thus a liquid might be imagined to be produced from a solid by the removal of certain atoms and the subsequent rearrangement of the remaining atoms to fill as nearly as possible the gaps which were left. In gener-:al there is a 10% increase in volume in passing from the crystalline to the liquid condition and the liquid state is characterised by a lack of the long range order which exists in crystalline material.

In the application of the reaction rate theory, Eyring has postulated that the activated molecule or molecules require greater volume than in the normal config-:uration. Since the energy of vaporisation $\Delta E_{vap.}$ is the energy required to form a hole of molecular size in the liquid, then the energy required for the extra volume of the activated complex may reasonably be related to $\Delta E_{vap.}$. This type of approach is only valid, of course, if the unit of flow is similar to the units existing in the vapour state of the substance.

Working on this basis Eyring found a constant ratio of $\frac{\Delta E_{vap.}}{E_\eta}$ of approximately 3 for a large number of liquids of the non polar class. This constant ratio indicates the validity of this type of approach and also tends to indicate that for these liquids the free volume is the important criterion in determining the viscosity of the liquids. That this is so is supported by the fact that the energy of activation for these liquids at constant volume is a small fraction of that at constant pressure. No great forces exist between the molecules of such liquids and hence little energy is required to move from one equilibrium position to another. The equation $\eta = Ae^{E_\eta/RT}$ holds well for these liquids and A and E_η are constant provided the temperature range is not too great. Eyring makes the reasonable approach that the process will take place through an activated state requiring the minimum extra volume. In a simple molecular liquid Stearn and Eyring(24) have shown that this would be achieved by the temporary formation of double molecules during flow.

Variations in the relationship of E_η to $\Delta E_{vap.}$ arise when more complex liquids are considered. Thus in ionic liquids e.g., KBr $\Delta E_{vap}/E_\eta$ is in the region of 4 and in $CdCl_2$ has a value of 7.9. While this does not indicate any departure from the dependence of viscosity on free volume it does indicate a more complex flow process. Thus in $CdCl_2$ evidence exists for the formation of auto complexes in liquid $CdCl_2$ which are dissociated on vaporisation.

This would explain the change in $\frac{\Delta E_{VAP.}}{E_\eta}$. It does become apparent on increasing the field of application by Eyring's method that more complex relations are taking place in the viscous flow of more complex liquids and a consideration of the relationship to $\Delta E_{VAP.}$ becomes of diminishing value. This becomes extreme in the case of silicate liquids which are ionic and which possess a considerable degree of highly directional bonding.

Making assumptions as to the nature of the activated complex, e.g., unimolecular reaction, i.e., movement of single molecules, and utilising an expression for the free volume of the liquid, Eyring derived the following equation to express the viscosity of a liquid

$$\eta = 1{\cdot}09.10^{-3}\,\frac{M^{1/2}\,T^{3/2}}{V^{2/3}\,\Delta E_{VAP.}}\,e^{E_\eta/RT}$$

where M = Molecular Weight. V = Molar Volume.

The pre-exponential term of this however differs from experiment by a factor of 2 to 4. Similarly in consider-:ation of the equation

$$\eta = \frac{h\,N}{V}\,e^{\Delta G/RT}$$

it is found that it also does not satisfy experimental data and differs by a constant similar to the exponential term above. Thus for CCl_4 the η calculated and the η observed differ by a factor of 2.0.

In the application of the equation $\eta = Ae^{E_\eta/RT}$ to associated liquids it is found that variations also exist. An example of this type of liquid is water which is assoc-:iated by hydrogen bonding. In such liquids E_η is

found to vary with temperature, i.e., the relationship $\log \eta \sim 1/T$ is non linear. Eyring explained this by the fact that a structural activation energy is required in addition to the volume energy increment for viscous flow. This is reflected in the more correct form of the equation

$$\eta = A' e^{-\Delta S/R} e^{\Delta H/RT}$$

by a higher value of ΔS i.e., increased entropy due to structural breakdown. The number of hydrogen bonds to be broken will decrease with increase in temperature and hence a decrease in the observed energy of activation E. It may be noted here that Bernal(25) has shown that configurational changes take place in water as the temperature alters and he considers that this change in configuration is responsible for the variation in E_η.

This variation in the energy of activation for viscous flow with temperature is shown by a large number of liquids not only by associated hydrogen bonded liquids, e.g., water and alcohols, but also by those ionic liquids which have structural bonding. Thus silicate melts in the truly liquid or in the glassy condition may show this property. As pointed out by Ward(22), the viscosity equation then becomes

$$\eta = A(T) e^{E(T)/RT}$$

and attempts have been made to find the theoretical form of this equation. (E.W.Madge)(26). Any attempt however has resulted in the use of three or four empirical constants so that this problem is unsolved.

The rather specific model of approach of Eyring is therefore untenable when applied to a large variety of liquids and a more general treatment is necessary to achieve a better understanding of the viscous flow of liquids as a whole. This is provided by the configuration theory of Bernal(18) and its development as applied to viscous flow by R.M.Barrer(19). Bernal considers that the free energy of the liquid is determined by the config-:uration of the units composing the liquid. From a consideration of the distribution functions of the mole-:cules Bernal has shown that the characteristic of the liquid state is the existence of points of abnormal coordin-:ation. This abnormal coordination prevents a continuous transition from the liquid to the crystalline arrangements. Frankel(1) considers the formation of a liquid to be associated with the loss of long range order and combining this with the configurational approach of Bernal, it can be seen that irregularity of configuration must exist in the liquid state.

Bernal has classified liquids depending on whether the effect of the units of the liquids on one another falls off slowly or quickly with distance. In the former case irregularity will be low and coordination number high. Non-polar liquids would belong to this group. In ionic liquids, however, due to the association of ions with ions of opposite sign the mutual potential falls of rapidly with distance. Here coordination will be low and irregularity higher. Viscous flow involving a change from

a normal configuration through an activated configuration to a second normal configuration will be associated with greater energy for low coordination. That is why the energy of activation for ionic liquids is greater than for simple liquids. In silicate liquids when the coordination may be as low as four this effect will be greatly augmented and thus result in higher viscosities. The greater the variety of ionic species present in an ionic liquid the greater the irregularity in the coordination of the liquid. This results in more complex relations taking place in the process of viscous flow.

R.M.Barrer(19) has combined the configurational approach of Bernal with the Arrhenius type equation

$$\eta = A e^{E_\eta/RT}$$

in his "zone theory of viscous flow". In this, the process of flow is associated with a zone of activation within the liquid, the zone being loosened by the absorption of energy of activation E_η. The zone itself is not regarded as moving but undergoes a loosening and configurational change constituting a unit act of flow. Large zones of activation are associated with high energies of activation. The term A takes account of the size of the moving units and also all effects of cooperation between units necessary for the flow process. Barrer has clarified the nature of this latter point by postulating that the entropy of activation consists of two terms:

(1) A positive component which varies with E_η, the energy of activation. The positive component may be associated with the structural breakdown before flow as it occurs in some liquids such as water. This may alter with temperature.

(2) A negative component depending on the amount of synchronisation or cooperative effort required for a successful unit act of flow. This will be dependent on the configurational arrangements in the liquid.

In normal non polar liquids, the normal configuration and the activated configuration will be very similar and in such cases ΔS will be zero or nearly so. Also the config-:uration is unlikely to change with temperature and so the relationship $\eta = A e^{E_\eta/RT}$ is obeyed where A and E are constant. In ionic liquids which will probably involve ionic clusters the configurational relationships are more involved and ΔS acquires a higher value. In polymerised ionic materials such as silicate glasses or basic oxide-silica melts of acid composition still more complex relationships are involved in the flow process. Here the effective coordination is low and irregular and changes with temperature and composition.

Consideration of the liquid state in general therefore shows that there is a large variation in the behaviour of liquids with change in constitution. At the one extreme are the simple non polar liquids in which the viscosity is

mainly dependent on free volume. Increasing complexity brings increasing interdependence of the constituents of the liquid and other factors being to dominate the contributions to the viscosity of the liquid. This may reach an extreme in polymerised melts in which a complex combination of structure and configurational change may be taking place during the process of flow.

VISCOSITY OF SLAGS AND GLASSES.

Many types of liquid have been examined and classified according to their viscous behaviour. In a similar manner slags can be examined on the basis of the theories previously discussed to find if they fit into the existing classification or if in fact they form a new class. With this purpose in view a systematic study has been made of a related group of slags with reference to the following variables:

(1) Change of viscosity with change of temperature.

(2) Effect of variable shear rate on viscosity.

(3) Change of viscosity with composition.

(4) Change in the thermodynamic functions for viscous flow with change in composition.

In addition consideration is given to the mechanism of flow in these liquids and to the form of the log $\eta \sim 1/T$ relationship in supercooled melts.

Investigations on the above basis will yield information on the constitution of these liquids, on the energies involved in the flow process and the change of these energies with composition. Tempered with the knowledge in other fields of work the reasons for the change in viscosity with the above factors can be deduced.

Little information is already available, however, in this respect since the early work on the viscosity of slags and glasses has been concerned mainly with materials of commercial composition. (McCaffery and co-workers(27) on $CaO-Al_2O_3-SiO_2$ slags of blast furnace composition and

S. English(28) on glasses). These are necessarily complex and little information regarding the effect of various constituents on the constitution of the liquid and on the process of flow can therefore be obtained from them. Practical difficulties have also retarded progress in this field and resulted in a scarcity of data which are sufficiently reliable to yield fundamental information.

In this respect work on the viscosity of glasses has until recently been of a higher standard that that on slags. This is well illustrated in the work of H.R.Lillie(29) on glasses and is undoubtedly due in large part to the greater experimental difficulties involved in slag viscosity. The necessity to work at high temperatures up to at least 1600°C and the very corrosive action of slags on the few materials available for use at such temperatures are the main difficulties. This latter point is important since viscosity is a property which is susceptible to the presence of impurities.

For this reason refractory oxides are generally unsuitable and the containers usually employed have been refractory metals and carbon. It has been generally accepted that carbon could not be used in contact with iron or manganese-containing slags, but that it was safe for lime silicates and lime aluminosilicate slags. Many viscosity measurements of such slags have in fact been carried out in carbon. Recently, however, some evidence of interaction between a lime alumina-silica slag and graphite has

been given by Towers(30) by contact angle measurements. Reduction of SiO_2 by carbon proceeded rapidly at temper-:atures above 1500°C but it also occurred slowly from the melting point up to 1500°C at very low partial pressures of CO. The effect on viscosity values will probably be slight up to 1500°C but may well be significant at higher temperatures. Results obtained under such conditions must therefore be viewed with caution particularly with respect to changes in composition. In general, however, little trouble is experienced with the CaO-MgO-SiO_2 type of slag but manganese silicates and iron silicates present special problems. It is known qualitatively that the behaviour of slags in the MnO-SiO_2 system differs in crucibles of different metals and they are also susceptible to slight changes in atmosphere. Even in the present investigation where precautions were taken, the accuracy of the results for MnO.SiO_2 are considered to be slightly lower than for other slags.

No single previous investigation has included all the factors listed earlier which are of interest in the viscous properties of silicates. Indeed the changes of viscosity with composition and with temperature have occupied most attention. A short review of the most important work with regard to these factors is thereforegiven.

Matsukawa(31) investigated the viscosities of a number of synthetic slags. The results were not expressed in absolute units of viscosity but the relative results are

not without value. Replacement of one metal oxide by another showed that the effect of various oxides in reducing the viscosity of the slags examined was in the order FeO > MnO > CaO and MgO. No great difference could be observed in the viscosity when lime replaced magnesia. The slags examined by Matsukawa were of complex composition in that they contained CaO, MnO, MgO, Al_2O_3 and SiO_2. Conclusions based on them therefore cannot be of universal validity. Thus the effect of an ion may be reversed depending on the composition of the melt. This is illustrated by considering simple silicates and aluminosilicates. As pointed out by Stanworth(6) the latter show increasing viscosity MgO → CaO → BaO which is the reverse of the order in simple silicates at least at high temperatures.

Investigations by Rait and Hay(32) and by Rait, McMillan and Hay(33) were the first real attempts to investigate the viscosity of slags from a systematic point of view. Using a rotating cylinder viscometer and graphite cylinders, they examined mainly lime-silica and lime-alumina-silica slags. For a given lime:silica ratio alumina had the effect of increasing the viscosity of the melt and the viscosity composition isotherms showed discontinuities as the composition changed from one field of primary crystallisation to another. Thus when the composition changed from the field of SiO_2-CaO.SiO_2-CaO.$Al_2O_3$2SiO_2 to CaO.SiO_2-CaO.$Al_2O_3$2SiO_2-2CaO.Al_2O_3.SiO_2 the isotherm showed a discontinuity becoming steeper in the latter field of

crystallisation. Isotherms within a field showed no such discontinuities . These results were taken to indicate the existence of complexes at high temperatures in the liquid, the complexes being related to the crystallising structure.

Great interest is also attached to the very marked minimum observed by Rait, McMillan and Hay(33) at the composition $CaO.SiO_2$. This was in contradiction to the results of Rait and Hay(32) who reported no minimum but rather a smooth continuous function between viscosity and composition. Indeed the occurrence of a minimum value at the compound composition $CaO.SiO_2$ has been a point of con-:troversy for some time. Thus Herty(34) and Rait, McMillan and Hay(33) report a minimum value at $CaO.SiO_2$ while R.S.McCaffery(35), Heidtkamp and Endell(36) and Rait and Hay(32) observed no minimum. The results of Herty are about 150% higher than those of the other workers. These of McCaffery, Heidtkamp and Endell, and Rait and Hay show fair agreement.

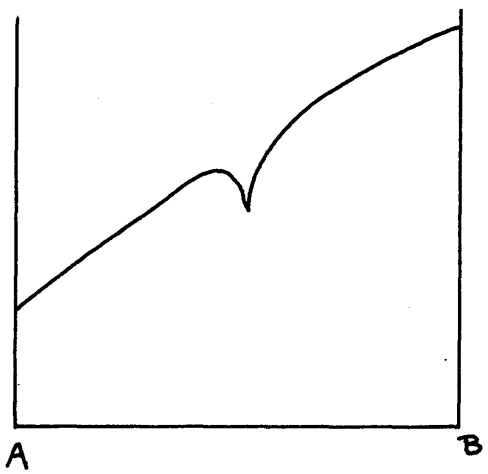
The controversy regarding minima in viscosity curves is not confined to lime silica slags but also exists as a result of work on Na_2O-SiO_2 glasses. E.Preston(37), using a rotating cylinder viscometer, reported results in Na_2O-SiO_2 glasses up to a temperature of 1400°C. These indicated a minimum at the composition $Na_2O.2SiO_2$ and a less definite minimum at $Na_2O.3SiO_2$. In addition the

recorded minima became more marked at higher temperatures. This system was reexamined in a careful investigation by H.R.Lillie(29) whose results agreed well with those of Preston except that no minima were recorded. Previous to Preston, Heidtkamp and Endell(36) had published results on this system showing no minimum although their data were too widely spaced to indicate conclusively the absence of a minimum value at $Na_2O.2SiO_2$. Preston explained his results by postulating the formation of complexes between end members of the systems SiO_2 - $Na_2O.2SiO_2$ and $Na_2O.2SiO_2$-$Na_2O.SiO_2$ so that a maximum appeared in the system $Na_2O.2SiO_2$ - $Na_2O.SiO_2$. At the disilicate composition no complexes were possible. This in effect postulates the existence of $Na_2O.2SiO_2$ in the liquid state and that such a molecule takes part in the flow process as a unit.

Heidtkamp and Endell(38) criticised the results of Preston mainly on the basis of the increasingly marked minimum as the temperature is raised. If such a compound as $Na_2O.2SiO_2$ existed in the liquid state the minimum would be expected to decrease in significance at higher temper-:atures due to dissociation of any complexes which may exist.

The approach made by Preston on the basis of his results i.e. considering a maximum between $Na_2O.2SiO_2$ and $Na_2O.SiO_2$ rather than a minimum between Na_2O and SiO_2, is

undoubtedly the correct one. No maxima or minima have been reported for a true binary system where the values are smaller or greater respectively than that of the components from which they were derived. That is, a curve as indica-:ted below has never been observed in a system A - B in which no compounds exist between A and B.



Thus in the $CaO-SiO_2$ system, the point of consideration would be a maximum between $CaO.SiO_2$ and $2CaO.SiO_2$ rather than a minimum at $CaO.SiO_2$. Many maxima have been reported in the literature on viscosity. In some cases a very marked maximum does occur at a compound composition. Thus the system stannic chloride-acetic acid shows a maximum at $SnCl_4.3CH_3.COOH$ the value of which is 263 times the viscosity of acetic acid. The occurrence of such a maximum whose position remains unaltered with temperature, is truly significant and is good evidence for the existence of such a compound. In many other systems however, e.g.,

ethyl alcohol-water, acetic acid-water, the maximum is more gradual and occurs at an indeterminate point between the components, and the point at which it occurs changes with temperatures. An explanation for this is less readily available and complex formation has been suggested between the end members of the system. In this respect however the approach of McLeod has been successful. McLeod has pointed out that many systems showing such maxima, e.g., ethyl alcohol - water, also show contraction in volume on mixing the two components and that the viscosity maximum corresponds to the maximum contraction of the system. This is undoubtedly an important observation and indicates the great dependence of viscosity on free volume for these liquids.

The maximum observed by Preston in the $Na_2O:SiO_2$-$Na_2O.2SiO_2$ system and by Rait, McMillan & Hay in the $CaO.SiO_2$ - $2CaO.SiO_2$ system therefore belong to the second type. Two explanations are therefore possible.

(1) That a contraction in volume occurs at some point between the end members. This would only be effective if the free space were the dominant factor in the viscous properties of these liquids.

(2) That the molecules $Na_2O.2SiO_2$ and $Na_2O.SiO_2$, exist and move as units within the liquid. Between compositions these molecules are hindered in their movement due to complex formation and hence a maximum occurs in the viscosity isotherm. This was the explanation given by

Preston and will be considered later with reference to the results obtained in the present work.

Machin and Hanna(39) and Machin and Tin Boo Yee(40) investigated $CaO-Al_2O_3-SiO_2$ slags and $CaO-MgO-Al_2O_3-SiO_2$ slags using a logarithmic decrement apparatus. This work confirmed the influence of Al_2O_3 in causing increased viscosity for a given CaO/SiO_2 ratio. The influence of MgO on these quaternary slags was to cause a reduction in viscosity.

Kozakevitch(41) investigated the viscosity of binary $FeO-SiO_2$ slags up to temperatures of 1400°C using iron cylinders. In this a very small maximum value was observed at $2FeO.SiO_2$ and Kozakevitch expressed the view that no great significance should be attached to the occurrence of this maximum value. In a later investigation(42) results were given for the ternary systems $FeO-CaO-SiO_2$ and $FeO-MnO-SiO_2$. No evidence was found in the form of maxima or minima for the existence of compounds $FeO.CaO.2SiO_2$ or $FeO.MnO.2SiO_2$ although in the system $FeO-CaO-SiO_2$ the surface of equal viscosity seemed to form a plateau in the region of the compound $FeO.CaO.2SiO_2$. In a later publi-:cation Kozakevitch(43) suscribes to the view that the occurrence of a maximum at a compound composition cannot be taken as indisputable evidence for the existence of a compound in the liquid state and also that on the basis of

the silicate network theory such maxima would not be expected. In the examination of the metasilicate joins, Kozakevitch showed that the replacement of FeO by CaO or by MnO caused increased viscosity.

In recent times, Shartsiss, Spinner and Capps(44) have measured the viscosity of Na_2O, Li_2O and K_2O silicate glasses up to 1400°C. Their results are in agreement with those of Lillie(29) for Na_2O-SiO_2 glasses. They showed that the order of increasing viscosity at high temperatures is Li → Na → K.

It can be seen therefore that the change of viscosity with composition on these silicate systems has been the main point of interest. Few attempts have been made to make any theoretical interpretation of the results. In the present work, the viscous properties of the silicate liquids have been investigated on the basis of the factors listed previously and a brief indication is given below of the information expected from such an investigation.

(1) Change of Viscosity with Temperature.

From the Arrhenius equation $\eta = A e^{E_\eta/RT}$ the energy of activation for viscous flow E_η, can be obtained from the plot $\log \eta \sim 1/T$. The magnitude of E_η gives an indication of the energies involved in the flow process of silicate liquids compared to other types of liquid. A non linear $\log \eta \sim 1/T$ relationship indicates that structural changes are taking place with change in temper-

:ature . The change of E_η for a given silica content with change in metal oxide gives information on the constitution of the melt and the effect of various ions on the silicate structure.

(2) Variation of η with variable rate of shear.

The viscosity of a liquid is given by the equation $\eta = \gamma/\sigma$ where γ = stress in dynes/cm^2 and σ = Rate of shear in cm/sec/cm. Investigations by Towers and Kay(45) indicate that for manganese silicates at least, the viscosity is a variable with the rate of shear.

(3) Change of Viscosity with Composition.

The viscosity of all silicate systems, whether in the truly liquid or in the glassy state increases with increase in silica content and moves to a maximum in pure silica. This is readily attributed to the strong direct-:ional bonding which exists in liquids of high silica content. The main point of interest here is the form of the $\eta \sim MO/SiO_2$ curve and the occurrence of maxima, minima, points of inflexion or changes in direction.

The change in viscosity with a change in composition involving the replacement of one metal oxide by another at a constant silica content can also be considered. The effect of an added oxide MO is to increase the coordination of the liquid and so cause a reduction in viscosity. The ability to do this differs for different metal oxides. This is related to the ionic strength of the metal ion

and hence a relationship between η and ionic strength can be obtained.

(4) Variation in the Thermodynamic Functions for viscous flow with change in composition.

The free energy of activation for viscous flow can be obtained from the equation

$$\eta = \frac{hN}{V} e^{\Delta G/RT.}$$

and the change in this can be observed with change in composition. The entropy of activation ΔS can also be obtained from the equation

$$\Delta G = \Delta H - T\Delta S$$

where ΔH = Heat of activation.

An increase in the value of ΔS i.e., an increase in the positive component of ΔS with change in composition indicates an increasing degree of structure within the liquid. In such a case, the heat of activation increases while the free energy of activation remains relatively constant. This increasing structural effect may arise as a result of a decrease in temperature or change in composition towards lower effective coordination in the liquid.

P A R T 3.

Methods of Measuring Viscosity.

The measurement of slag viscosities involves practical difficulties which rule out many of the established methods of viscosity measurement. The principal methods are discussed below and the reasons for choice of method indicated.

(a) Capillary Method. This is the most widely used method for work at room temperatures. Liquid is forced through a capillary of accurately known dimensions and the volume discharged in unit time is measured. From a knowledge of the pressure used, the dimensions of the capillary and the volume obtained, the viscosity can be calculated. This method has the advantages of simplicity, small volume of liquid required, easy control of uniform temperature throughout the liquid, and a rigid mathematical theory. At high temperatures, however, for the measurement of slag viscosities, the difficulty of controlling and observing the movement of a given volume of molten slag and of maintaining the temperature constant over a capillary of reasonable length, makes this method practically invalid for accurate work. This is made even more so by the necessity to adjust the volume of liquid at each temperature In spite of these difficulties, however, some use has been made of the method in the measurement of metal viscosities up to 600°C. by R. Lorenz and H.T.Kalmus(46).

(b) Falling Sphere Method. This method utilises a relationship due to Stokes in which the viscosity of a medium may be derived from the velocity of fall of a sphere through the liquid medium.

$$\eta = \frac{2r^2(\rho - \rho')}{9V} g$$

r = Radius of Sphere ρ and ρ' = Density of sphere and liquid respectively.

g = Gravity Constant V = Observed velocity of fall.

This equation is only applicable if the liquid is of infinite extent with respect to the sphere and so it cannot be satisfied experimentally. To take into account the effect of the walls of the containing vessel, R.Landenburg(47) introduced a correction. For an infinitely long cylinder the formula becomes

$$\eta = \frac{2r^2(\rho - \rho')}{9V(1 + 2.4r/R)} g$$

R = Radius of cylinder

provided the condition $R = \frac{r\rho V}{\eta}$ is also observed. Landenburg also introduced a correction for the effect of the ends of the containing vessel. For accurate work by this method therefore, the volume of liquid must be considerably greater than that of the sphere and this condition is its main disadvantage in slag work. It is very difficult to maintain large volumes of slag at a uniform temperature in the region of 1600°C. The difficulty of observing the fall of the sphere is another disadvantage although this has been successfully overcome in the measurement of glass viscosities by A.R.Wood(48)

by the use of X-rays. Other workers have used the method for the measurement of glass viscosities, e.g., Stott, Turner and Sloman(49) by suspending the sphere in the glass from a wire attached to a balance beam. Various loads were then applied to the opposite end of the beam and the velocity of the sphere observed.

(c) Logarithmic Decrement Method. In this case viscosity coefficients are determined from the observed oscillations of a suspended unit in the liquid medium. The suspended unit may consist of a disc, a sphere, or a cylinder, suspended in the liquid from a torsion wire. The mathe-:matical theory of this method is extremely involved and introduces approximations. According to Hatchek(15), room temperature work shows considerable deviations from other standard methods.

Oscillations are observed and viscosity coefficients are calculated from the relationship

$$\eta = \frac{\sqrt{DI}}{K\pi} \log_e p$$

where p = Ratio of two successive amplitudes - $\log_e p$ must be small.

D = Torsion characteristic of suspension.

I = Moment of Inertia of suspended system.

K = Apparatus constant calculated from the dimensions of the apparatus.

This method is suited to high temperature work for slag measurements since it has the advantage of requiring only a small volume of liquid and therefore makes possible the maintenance of a uniform temperature throughout the slag

bulk. It also has the advantage that the apparatus required is comparatively simple in design. Heidtkamp and Endell(36) and Rait and Hay(32) have used this method for the measurement of slag viscosities. These workers employed the oscillation of a suspended cylinder and calibrated the apparatus empirically at room temperature. No mathematical solution exists for the oscillation of a suspended cylinder in a liquid medium although approxima-:tions can be made from the case derived for the oscill-:ations of a suspended sphere provided that certain conditions are satisfied. Where this is so, the factor K may be taken

$$K = 4\pi h \frac{a^2 b^2}{b^2 - a^2}$$

h = Length of Inner Cylinder.

a = Radius of Inner Cylinder.

b = Radius of Outer Cylinder.

For the accuracy to be expected in high temperature slag viscometry, these approximations are justified and the method is particularly suitable for fluid slags.

(d) Rotating Cylinder Method. Margules in 1881 devised the concentric cylinder method for viscosity measurement in which an outer cylinder containing the liquid medium is rotated at constant speed and the torque produced on an inner cylinder measured by means of a torsion suspension. A modification of this may be made whereby the inner cylinder is rotated by an applied torque while the outer

cylinder remains stationary and the time of one revolution of the iner cylinder measured. This latter modification has been used by Rait and Hay(32).

The method has the advantages of a rigid mathematical derivation and also of employing only a small volume of liquid and thus allowing close temperature control. Although an apparatus based on this method is more involved in design than one on the logarithmic decrement principle, it has two advantages over the latter method of measurement.

(1) A very wide range of viscosities can be measured.

(2) Constant rates of shear can be applied to the liquid.

Viscosity measurements on water have been made by Gurney(50) in agreement with the values obtained by capillary methods. The method has also found application in rheological work in which the liquid systems are investi-:gated at different constant rates of shear(51)(52).

Application to high temperature measurements has proved successful and H.R.Lillie(29) has used this system for glass viscosities. R.S.McCaffery and co-workers(27) have also measured the viscosities of blast furnace slags by this method.

The rotating cylinder system was chosen as the most suitable method for the programme of work involved in the present research. This included an investigation into the viscous properties of liquid silicates at various constant rates of shear both in the truly liquid and in the super cooled state. For this the rotating cylinder system is the only practicable method for high temperature work.

The viscosity of silicate systems changes rapidly on passing from the truly liquid state to the supercooled state and the wide range of viscosity which this involves can only be accomplished with accuracy in a viscometer of the rotating cylinder type. In the design of the viscometer therefore the primary considerations have been

(1) That a range of shear rates be employed sufficient to give an observable change in viscosity in a liquid system where this might be expected.

(2) That the range of viscosity values which can be observed should be sufficient to allow measurements to be made on slags showing a high degree of supercooling.

Quite apart from any change in viscosity with change in rate of shear, the use of different rates of shear is a useful method of extending the range of any given viscometer. The points of consideration in the design and the description of the viscometer which has been built for the present work are given in a later section.

Theory of the Concentric Cylinder System.

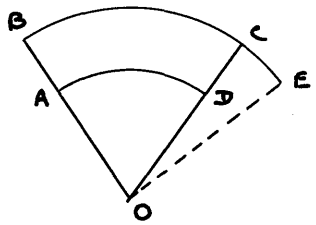
An exact mathematical treatment can be derived for the system consisting of two vertical coaxial cylinders between which a liquid is being sheared. The treatment given here appears to be originally due to Poynting and Thomson(53).

If the outer cylinder is rotated at constant speed, the liquid assumes a constant rotary motion which is communicated to the inner cylinder. The inner cylinder, suspended by a torsion wire, takes up a stationary position depending on the viscosity of the liquid medium. Under these conditions the constants of the system can be found and viscosity coefficients determined.

Consider a vertical length L of inner cylinder, of radius R_1 and suspended coaxially in an outer cylinder of radius R_2. Let the outer cylinder be rotated at constant angular velocity Ω. When a steady state has been reached, each circle of radius r ($R_1 < r < R_2$) will rotate with some constant angular velocity ω. That no acceleration may occur, then the moment of forces maintaining rotation must equal the moment due to viscous resistance.

Moment due to Viscous Resistance = Area x Velocity Gradient x Viscosity Coefficient x Radius.

The expression for the Velocity Gradient may be found as follows:



A and B are points on two of the concentric circles in which the liquid moves. In time "t" seconds, point A moves to D and B moves to E

Let OA = r. OB = r + Δr.

Angular Velocity of A = ω

" " " B = $\omega + \Delta\omega$

Velocity Gradient = $\frac{\text{Difference in Velocity between A \& B}}{\text{Distance between them.}}$

Linear Velocity of B = $(r + \Delta r)(\omega + \Delta\omega)$.

$= r\omega + \omega\Delta r + r\Delta\omega + \Delta r\Delta\omega$

$= r\omega + r\Delta\omega$ if Δr is small

Linear Velocity of A = $r\omega$

$\therefore$ Velocity Gradient = $\frac{r\Delta\omega}{\Delta r}$ when Δr is small

$= \frac{r\,d\omega}{dr}$

Thus the moment (M) due to viscous resistance

$$M = 2\pi r L \eta \, r \frac{d\omega}{dr} \, r$$

$$= 2\pi r^3 L \eta \frac{d\omega}{dr}$$

where r is any radius between the inner and the outer cylinder.

Integrating with respect to r

$$-\frac{M}{r^2} = 4\pi L \eta \omega + C$$

Substituting the boundary conditions at the walls of the cylinders

$\omega = \Omega$ $\quad r = R_2$

$\omega = 0$ $\quad r = R_1$ $\quad \therefore C = -\frac{M}{R_1^2}$

Thus $\frac{M}{R_2^2} = \frac{M}{R_1^2} - 4\pi L \eta \Omega$

$$\therefore M\left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right) = 4\pi L \eta \Omega$$

$$M = 4\pi \frac{R_1^2 R_2^2}{R_2^2 - R_1^2} L \eta \Omega = C \eta \Omega$$

where $C = 4\pi L \frac{R_1^2 R_2^2}{R_2^2 - R_1^2}$, an apparatus constant.

M is measured by the torsion (θ) of a wire of known restoring moment,

(K), from which the inner cylinderis suspended.

$$K\theta = M = C \eta \Omega$$

$$\therefore \eta = \frac{K\theta}{C\Omega}$$

$\Omega = 2\pi/t$ where t is the period (secs) of revolution.

K can be determined, as indicated in the calibration, by the oscillation of standard weights of known moments of inertia.

$$K = \frac{4\pi^2 I}{T^2}$$

I = Moment of Inertia of Standard Weight

T = Period of Oscillation.

The torsion angle(θ) can be determined by the reflection of a light source on to a scale set at a suitable distance from the apparatus. In this instance a straight scale was used and graphs were drawn, relating scale deflection against θ, the angle through which the inner cylinder is turned.

$C = \frac{4\pi R_1^2 R_2^2}{R_2^2 - R_1^2} L$ can be calculated from the

dimensions of the apparatus and can be corrected for expansions due to high temperature. Thus the expression for the coefficient of viscosity becomes

$$\eta = \frac{K\theta t}{2\pi C}$$

In practice, the inner cylinder is of finite length and some account must be taken of the viscous drag due to the ends of the cylinders. This may be done by calibrating against liquids of known viscosity or by measuring the apparent viscosity of a liquid with different lengths of inner cylinder. An extrapolation to $1/L = 0$ then gives the true viscosity of the liquid from which an equivalent length of inner cylinder can be calculated to account for end effects.

The velocity gradients or rates of shear for given values of Ω may be calculated as follows.

$$M = 4\pi \frac{R_1^2 R_2^2}{R_2^2 - R_1^2} L\eta\Omega = 4\pi \frac{R_1^2 r^2}{r^2 - R_1^2} L\eta\omega$$

$$\therefore \omega = \Omega \frac{R_2^2 R_1^2}{r^2 R_1^2} \cdot \frac{r^2 - R_1^2}{R_2^2 - R_1^2}$$

$$= \Omega \frac{1/R_1^2 - 1/r^2}{1/R_1^2 - 1/R_2^2}$$

$$\therefore \frac{d\omega}{dr} = \frac{2\Omega}{r^3} \frac{1}{1/R_1^2 - 1/R_2^2}$$

$$\therefore r \frac{d\omega}{dr} = 2\Omega \frac{1/r^2}{1/R_1^2 - 1/R_2^2}$$

The average rate of shear can then be calculated for

$$r = \frac{R_1 + R_2}{2}$$

PART 4.

DESIGN AND DESCRIPTION OF APPARATUS.

For the accurate measurement of the viscosity of a slag the first essential condition is that the volume of slag used should not be so large that the liquid cannot be maintained at a constant uniform temperature. The apparatus should therefore preferably be small. However, a compromise must be achieved between the small dimensions which are preferred for the above reason and the fact that cylinders of reasonable dimensions must be used in order that suitable deflections be obtained. The smaller the cylinders which are used, the greater the rates of shear which are required in order to obtain a deflection which can be observed with accuracy. In the present work the interest from the variable rate of shear aspect was to investigate the liquids at rates of shear lower than normal value of 0.7 sec.$^{-1}$ rather than greater. In addition, eccentricities of rotation are more serious for cylinders of smaller dimensions. The dimensions of the cylinders have been chosen therefore with these points in mind. An outer cylinder of Pt. 10% Rh. alloy of 1" diameter and 2" length has been used. A uniform hot zone of 2" can reasonably be achieved in a platinum resistance furnace at temperatures of 1600°C. Anything larger than this, however, would not be easily practicable since the dimensions of the furnace then required would be too great. An inner cylinder, also of Pt. 10% Rh. of 1" length and $\frac{1}{4}$" diameter has been used with a platinum connecting rod 1/16" diameter.

The viscous drag on the surface area of this rod in contact with slag is very small compared to that existing on the cylinder.

With such cylinders the annular space is 0.375", sufficiently large to prevent the cylinders touching should misalignment occur. If the cylinders did touch at a temperature of 1600°C instantaneous welding would occur. These dimensions, for the normal rates of shear used in viscometric work, give measurable deflections for the order of viscosity observed in slags at 1600°C. The lower values of viscosity measured in the slags examined are in the region of 1 to 2 poise. The dimensions of the furnace were based therefore on these cylinder dimensions. An inner mullite tube of $1\frac{1}{2}$" internal diameter was considered suitable and allowed rotation of the crucible system without danger of contact. The furnace tube was then fixed at 2" internal diameter.

The next point of consideration was the range of rates of shear which should be applied to the liquid. It was intended that measurements should be made at rates of shear varying from a normal value of 0.7 sec^{-1} to very low rates of shear and a range of shear rates, given later, was evaluated mainly on the basis of those existing in the work of Towers and Kay(45) on the $MnO-SiO_2$ system. It was decided that the best method of applying this would be by a friction drive system and that a high speed motor suitably geared down should be used. The essential

condition in the drive system to the viscometer is that the speed of rotation should be constant. Variable speed motors were not regarded as suitable due to their tendency to show fluctuating speed.

Phosphor bronze torsion tapes were chosen as the means best suited for the measurement of the deflection of the inner cylinder. These retain their torsion characteristics over a long period of time. It was necessary to use two tapes in series in order that reasonable deflections be obtained at all rates of shear and for a wide range of viscosities. The strength of the tapes necessary was therefore calculated on this basis and on the basis of using a graduated scale set at a distance of 1 metre from the suspension. In this case a straight scale has been used and the deflection of the cylinder then obtained from the tangent of the angle of deflection from the zero position.

The design of the apparatus has therefore been made on the basis of the considerations indicated above. As far as possible, simplicity has been adhered to in the experimental set up. One complicating factor has been the difficulty of providing a controlled atmosphere in such a rotating system. This was finally solved by the use of a "Gaco" seal ring which is of a rubber composition and which maintains a gas tight seal while bearing on a rotating metal surface. This is shown in the diagrams of the apparatus. The system is, of course, never completely

shut off from the air atmosphere due to the small hole at the top for the entry of the platinum spindle. However, as indicated later this did not prevent the successful use of a controlled atmosphere.

The final consideration is the method whereby the temperature of the slag is measured. Preston(37) has pointed out that the temperature measurement should be made at the point at which greatest shear is occurring. In the present system this occurs at the walls of the containing vessel. Temperature measurement was therefore made by a Pt-Pt.13% Rh. thermocouple situated at the base of the crucible. It was considered that any other arrangement for the measurement of temperature would introduce complications in the rotating system out of all proportion to the advantages gained.

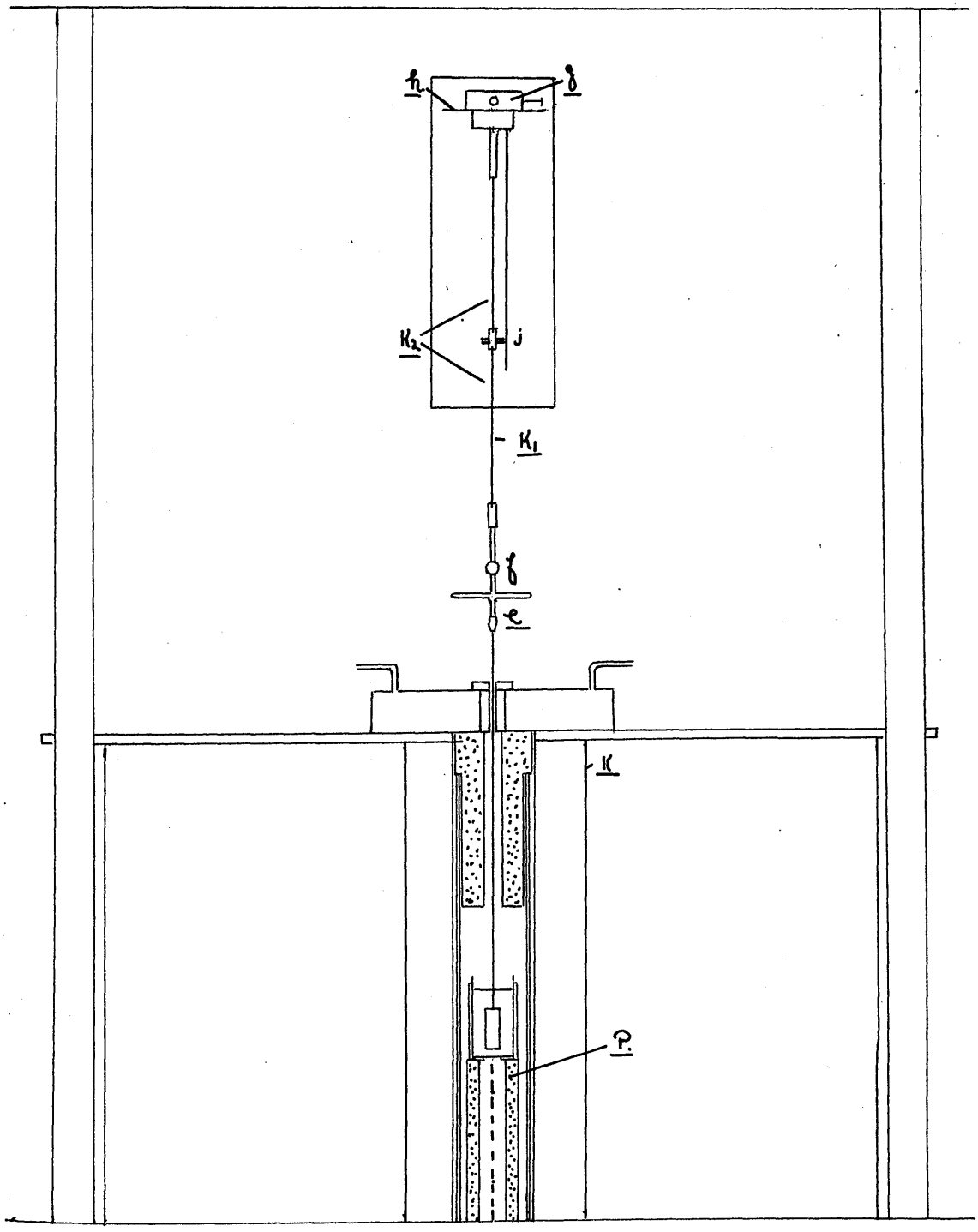
A diagram of the viscometer is shown in Figs.1A and 1B and photographs of the complete apparatus on the following pages. The design involves two major parts.

(1) A driving mechanism.

(2) A furnace system for measurements up to 1600°C.

(1) Driving Mechanism (Figs.2 and 3).

A speed of 1425 r.p.m. from motor A is reduced by a 15/1 worm reduction unit B. The output shaft from this enters gearbox C where the speed may be further reduced by a series of 2/1 reductions as follows. A diagram of the gearbox is shown in Fig.2. Shaft DEF may rotate as a



Frg 1A

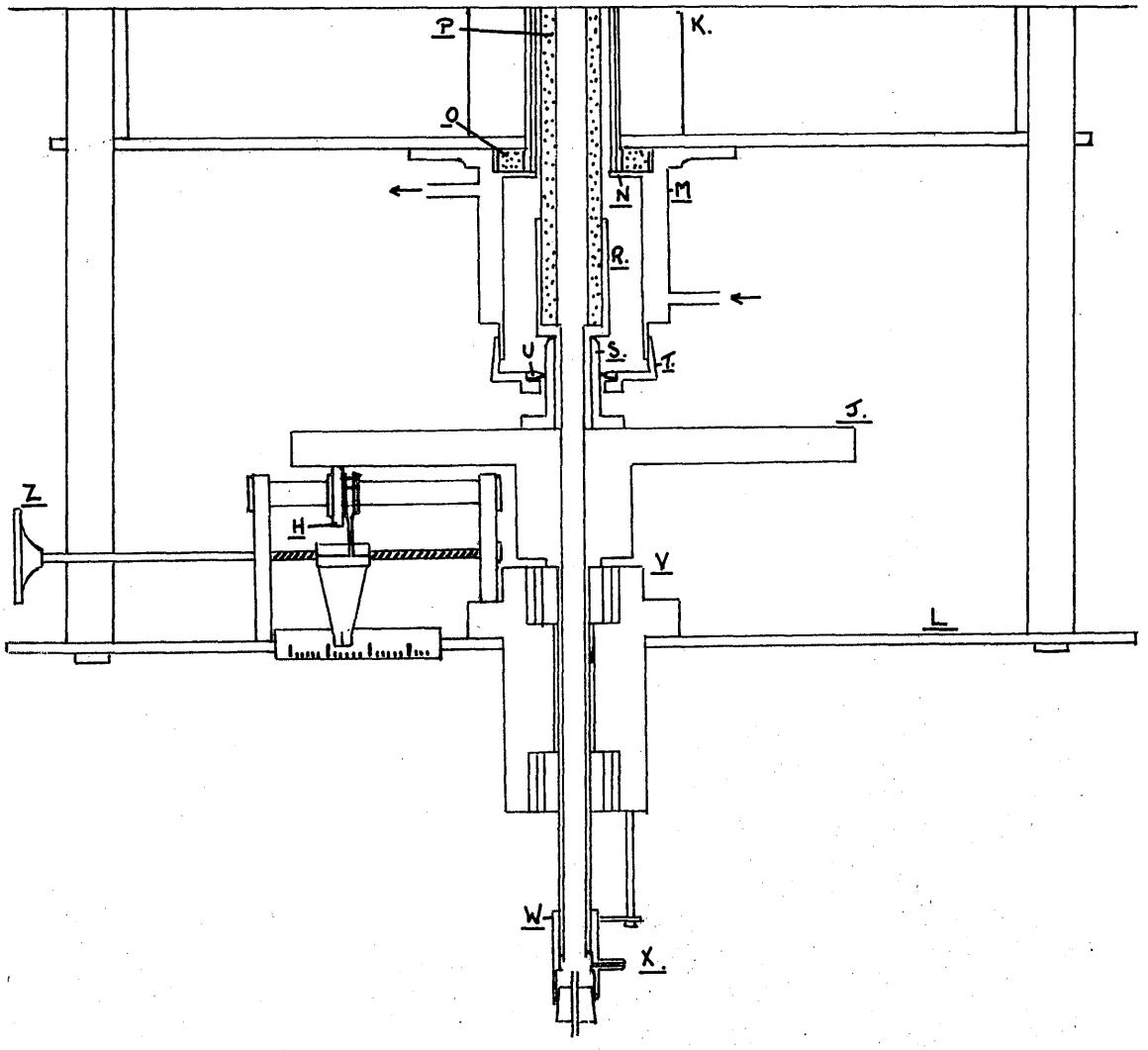


Fig. 1 B

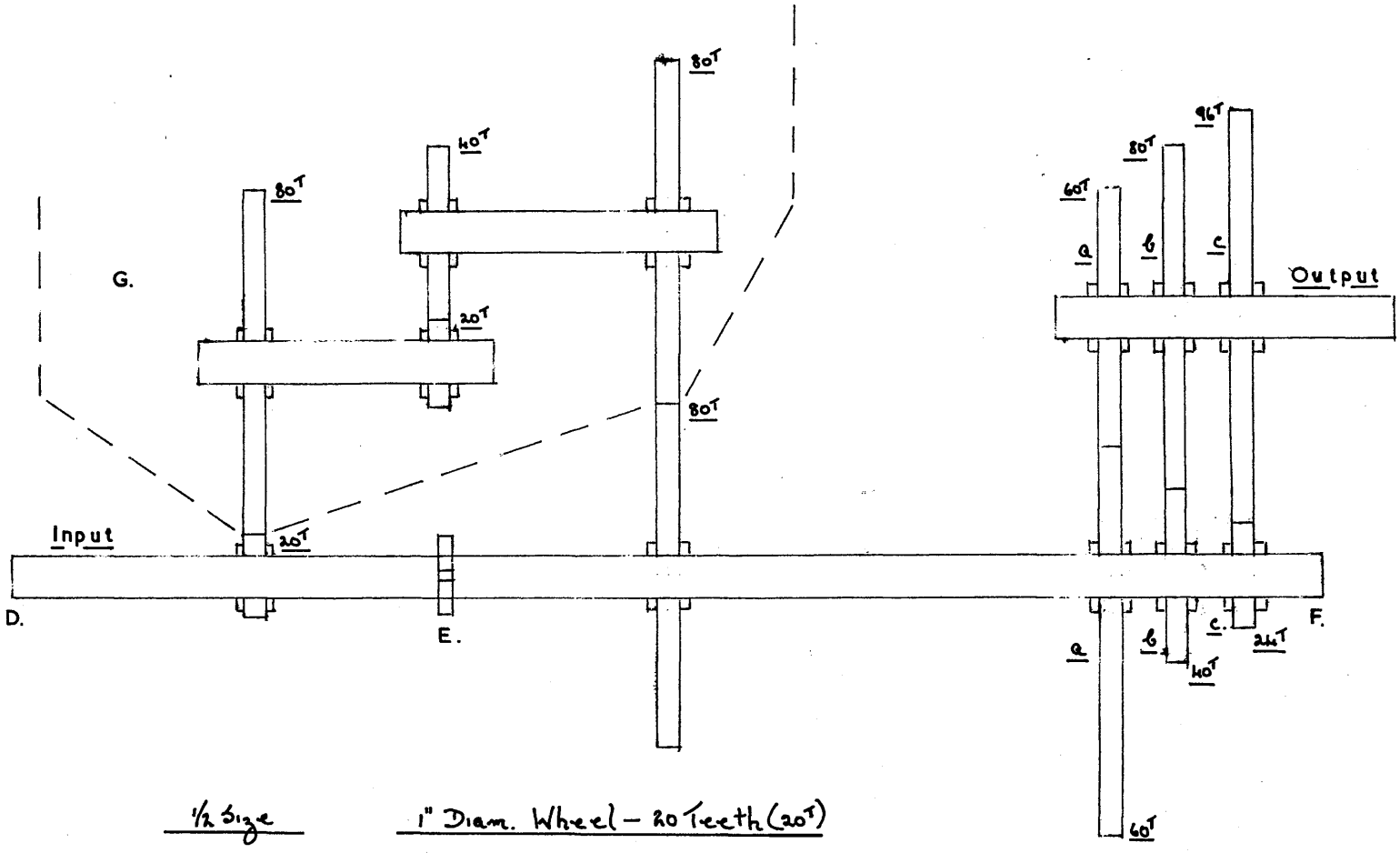
complete unit or as two separate units DE and EF by coup-:ling or uncoupling at E as desired. Spur gears (aa), (bb), and (cc) have reduction ratios 1/1, 2/1, and 4/1 respectively and any one may be engaged. Section G of the gearbox involves an overall reduction of 8/1 and is introduced to obtain the lower range of shear rates in which case DE and EF rotate independently.

A straight through drive of the 95 r.p.m. input shaft by means of (aa) gives maximum speed in the output shaft. This may be reduced by 2/1 - gears (bb) or 4/1-gears (cc).

By introducing section G and uncoupling at E, an 8/1 reduction is achieved by means of (aa) and further reductions 16/1 by (bb), and 32/1 by (cc), can also be made. Thus the output shaft can be varied from a maximum of 95 r.p.m. to a minimum of 3 r.p.m. by successive 2/1 reductions.

The output shaft is connected to a rubber drive wheel (H) ($1\frac{1}{4}$" diameter - Fig.IB) which operates by friction on the underside of the cast iron base plate J. (12" diameter). The drive wheel may be moved to any position on the outer 3" of the base plate radius. Thus by a movement of the drive wheel from the inner position (3" radius drive) to the outer position (6" radius drive) a 2/1 reduction in the speed of the base plate can be affected for any given speed of the drive wheel. In this way a complete range of speeds of rotation of the base plate can be obtained

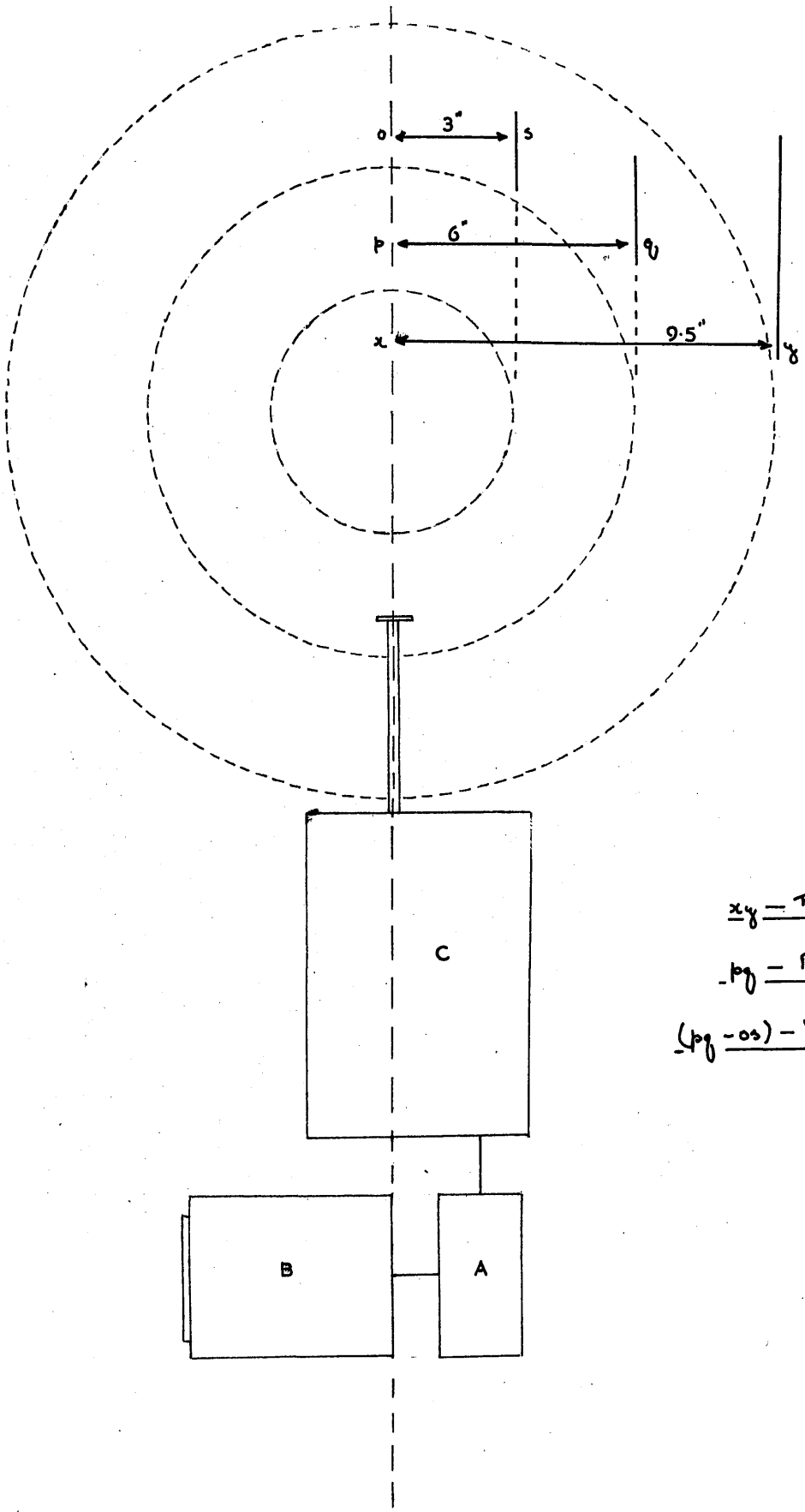
Fig 2



½ Size

1" Diam. Wheel – 20 Teeth (20T)

Fig 3



xy — Furnace Radius

pq — Base Plate Radius

(pq - os) — Working Range.

from a maximum of approximately 20 r.p.m. $(\frac{1.25 \times 95}{6})$ to a minimum of approximately 0.3 r.p.m. $(\frac{1.25 \times 3.0}{12})$.

From these speeds of rotation the rates of shear applied to the liquid have been calculated according to the formula

$$r \frac{d\omega}{dr} = \frac{2\Omega}{r^2} \cdot \frac{R_1^2 R_2^2}{R_2^2 - R_1^2}$$

where r = Any radius between the inner and the outer cylinder.

and taking $r = \frac{R_1 + R_2}{2} = 0.794$ cm. to give the average value.

R_1 = Radius of Inner Cylinder = 0.318 cm.

R_2 = Radius of Outer Cylinder = 1.27 cm.

Ω = Angular Velocity of the Outer Cylinder = $2\pi/t$

where t = period of 1 revolution - 20 r.p.m. t = 3 sec.

3 r.p.m. t = 200 sec.

t(secs).	(rads./sec.)	$r\, d\omega/dr$ (sec^{-1})
200	0.031	0.011
3	2.094	0.716

In practice, due to wear on the rubber drive wheel and slight variations in the speed of the motor, the speeds of rotation deviated slightly from the theoretical quoted above. The period of revolution was taken therefore each time and the measured value used in the calculation of viscosity.

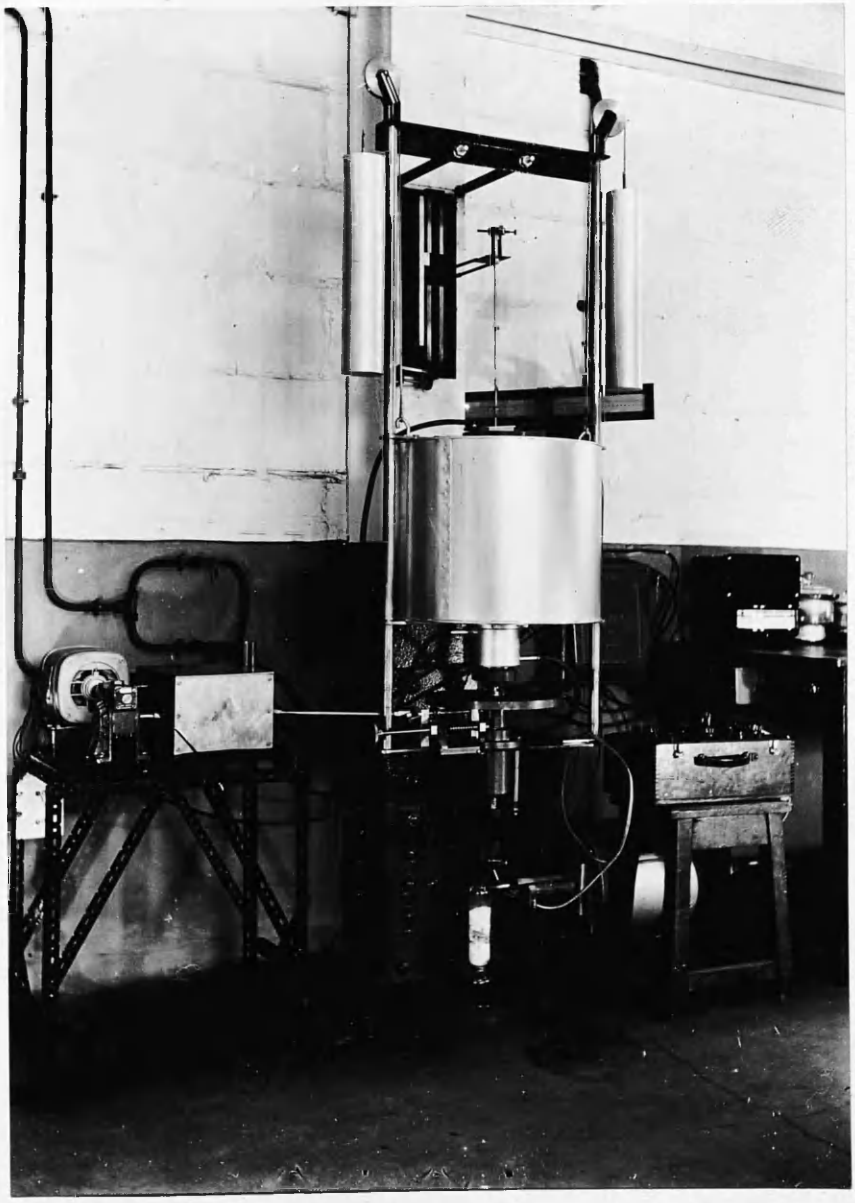
(2) Furnace.

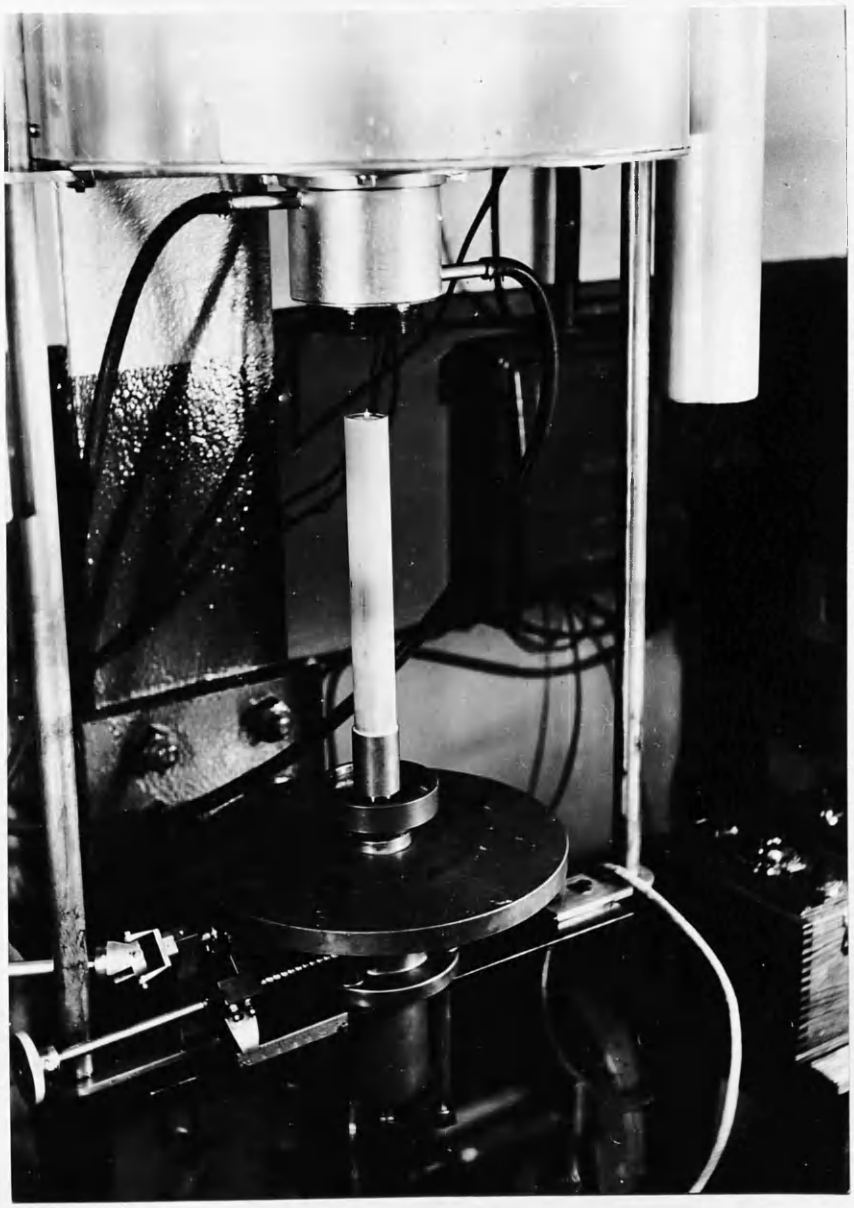
A diagram of the furnace is shown in Figs.1A and 1B. A resistance element of 18 gauge Pt 13% Rh. wire is wound over 13" of the 2" internal diameter winding tube. This is surrounded by a layer of crystallised alumina held in position by alundum tube K. (4" internal diameter). Insulating firebricks capable of withstanding 1500°C surround this tube and the remainder of the casing is filled with diatomaceous insulating bricks. The casing is of steel sheet with asbestos board ends - the total length being 15" and diameter 19".

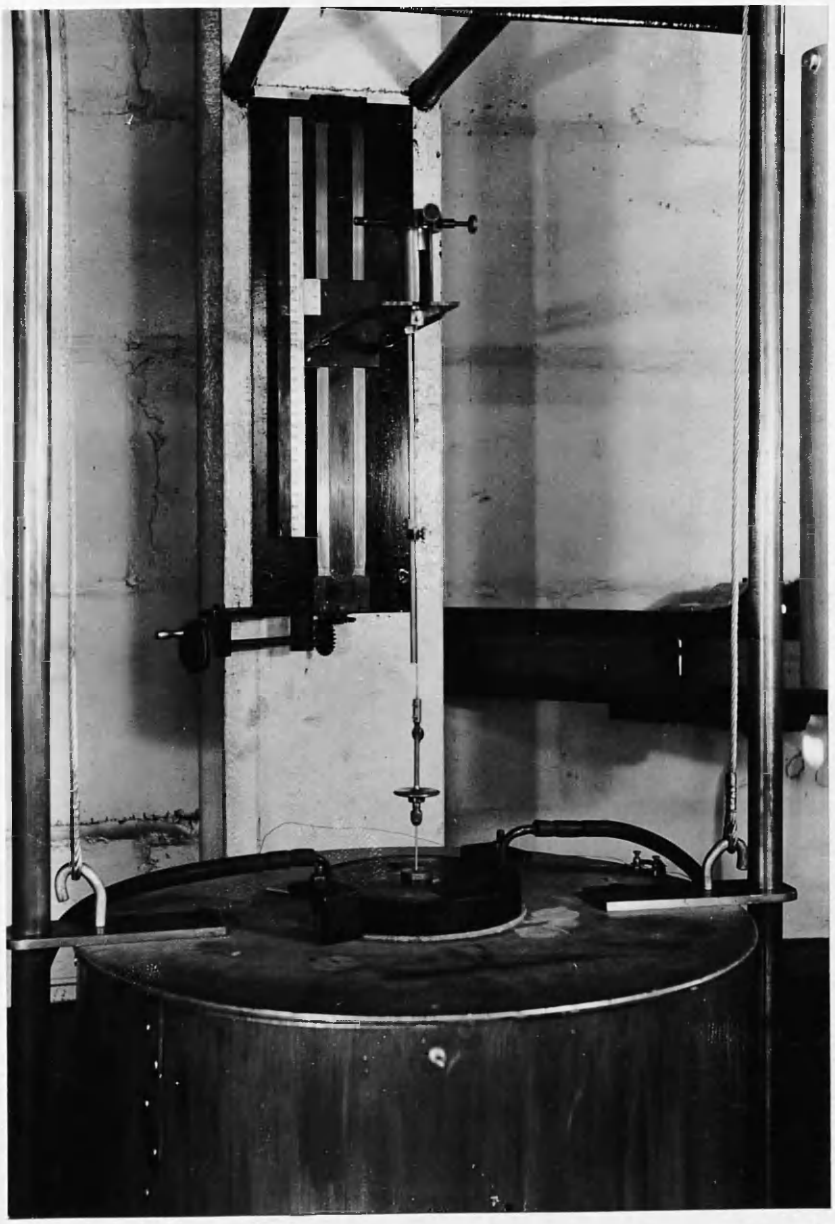
With the insulation as described above, a temperature of 1600°C was easily obtained and a maximum safe working temperature normally observed. Readings above this temperature were only taken on occasion when the melting temperature of the slag was such that only a narrow temperature range was available.

Determination of the furnace hot zone was carried out with as many components in position as possible and a variation of 4 centigrade degrees found over a 2" range at 1550°C situated 6"/8" from the furnace top.

The furnace is mounted on two vertical supports and is suspended over pulleys by lead weights. At the upper end the vertical supports are fixed to a cross bar and at the lower end to the horizontal table L. Both the crossbar and the table are fixed to a steel beam so that the viscometer itself is independent of any floor vibration.







To the table also are fixed the base plate J and the drive wheel system. Thus the furnace can be raised and access to the crucible easily made.

A water cooled metal casing M on the underside of the furnace is necessary to prevent warpage of the rotating components. Part of this casing is the metal plate N having a $1\frac{1}{2}$" diameter hole and on this plate rests the inside furnace tube of Mullite ($1\frac{1}{2}$" internal diameter). The metal plate N is separated from the furnace by an insulating alundum ring O.

An alundum spindle P with a $\frac{1}{2}$" central hole supports the platinum crucible on the hot zone of the furnace. At its lower end the spindle fits into cup R in the holder S. A seal is provided at this lower end by the screw cap T. This has a hard rubber ring U which fits neatly on holder S. In this way rotation of the spindle can occur without leakage to or from the atmosphere at this point.

Base plate J rotates in the bearing house V and the lower end of its spindle is fitted with cup W for the insertion of a thermocouple and the provision of a controlled atmosphere through X if necessary. Temperature is measured by the Pt-Pt.13% Rh. thermocouple situated immediately beneath the platinum crucible. During rotation of the system, the thermocouple, being fixed at W remains stationary. The drive wheel H operates on the underside of base plate J and its position may be altered by rotation of spiral screw Z. Temperature

control is maintained by means of a Kelvin Hughes Electronic Controller with a Pt-Pt 13% Rh. thermocouple situated in the hot zone between the inner mullite tube and the alundum winding tube.

A 4" long alundum insulating plug rests on the mullite furnace tube and a water cooled top protects the phosphor bronze suspensions K_1 and K_2. from heat. The water cooled top is fitted with two brass guides so that the platinum spindle may be accurately aligned. A brass chuch (e) for holding the spindle also adds weight to the suspension and is fitted with a small mirror (f) by means of which the deflection of the system is observed.

The suspension system hangs from the centring device "g" which rests on a movable platform (h). Movement of the platform is observed on a scale fixed to the wall so that the end separation of inner and outer sylinders can always be known. To the centring device is attached the clamp (j) by means of which the upper suspension can be brought into use as desired.

CALIBRATION OF APPARATUS.

The constant of calibration in the rotating cylinder system can be obtained by two methods.

(1) By calibrating with a liquid of known viscosity.

(2) By using a series of inner cylinders of equal diameter but different lengths and finding the end effect for the given cylinder diameter. In this method it is not necessary to find the viscosity of the oil being used by a separate means.

In this work both methods have been used and greater use has been made of the first. An accurate calibration using the second method alone would necessitate the use of a large range of inner cylinder lengths and diameters. The complete calibration involved three sections as follows.

(1) Torsion Characteristics of Suspension Wires.

Two phosphor bronze torsion wires were used and these were connected in series so that a suitable deflect-:ion could be obtained for any given viscosity or rate of shear. They were standardised by timing the oscillations of standard weights whose moments of inertia could be calculated. The torsion characteristic of the wire is given by

$$K = \frac{4\pi^2 I}{T^2} \text{ dyne cms/radian of twist}$$

where I = Moment of Inertia of oscillating weight ($gm.cm^2$).

T = Period of oscillation (secs.).

The moment of inertia of a cylinderical weight suspended along its major axis is given by

$$I = \tfrac{1}{2} M r^2$$

M = Mass (gm.) r = Radius (cm).

Four standard weights were employed, the data for which are as follows

Standard.	Mass.	Radius.	Moment of Inertia.
Brass Weight(H)	89.63 gm.	0.6350 cm.	18.07 gm.cm^2.
" " (L)	49.75 gm.	0.3175 cm.	5.61 " "
Aluminium Weight(H)	23.39 gm.	0.6350 cm.	4.21 " "
" " (L)	16.24 gm.	0.3175 cm.	2.03 " "

To these moments of inertia must be added that of a small brass connection rod holding the mirror by means of which the oscillations were timed by the reflection of a light source. This could be obtained by timing the oscillations of the different cylinders and substituting in the formula

$$\frac{(I_1 + x)}{T_1^2} = \frac{(I_2 + x)}{T_2^2}$$

where x = Moment of Inertia of the connecting rod, and I_1 and I_2, are known quantities. Results for the two torsion wires are given below.

Standard.	Period of Oscillation. K_1	K_2
Brass Weight (H)	1.27 sec.	2.589 sec.
" " (L)	0.717 sec.	1.467 sec.
Aluminium Weight (H)	-	1.287 sec.
" " (L)	-	0.917 sec.

These results gave the constants for torsion wires K_1 and K_2 as follows

	K_1	K_2
Brass Weights	445 dyne.cms/radian twist	108 dyne.cms/radian twist.
Aluminium Weights	-	107.7 " " "

(2) Standard Liquid of known Viscosity.

It was desirable that the liquid chosen for use in the rotating cylinder viscometer should have a suitable range of viscosities at ordinary temperatures. For this purpose castor oil was chosen as a suitable liquid and the viscosity of B.P. castor oil was determined over a range of temperature using the technique of capillary viscometry. The standard against which the viscosity was determined was that of a 60% sucrose solution, the viscosity of which was obtained from the International Critical Tables.

Kinematic Viscosity of 60% Sucrose Solution at 25°C = 0.3511 Stokes. Three viscometers were used in the determination of the viscosity of the castor oil

(a) An Ostwald Viscometer.

(b) Institute of Petroleum Viscometer No.3.

(c) Institute of Petroleum Viscometer No.4.

This was necessitated by the fact that the sucrose solution and the castor oil solution could not be run in the same viscometer due to their widely differing viscosities. Thus a transposing liquid had to be employed and a 90% glycerine ~ 10% water solution was

chosen for this purpose. This was prepared and stored in a tightly stoppered flask since the solution tends to absorb moisture.

The relationships involved in the calculation of viscosity by this method are as follows

$$\frac{\eta_s^t}{\eta_g^t} = \frac{\rho_s^t \; t_s^t}{\rho_g^t \; t_g^t}$$

where η_s^t = Viscosity of sucrose solution at temperature t °C.

η_g^t = " " glycerine " " " "

ρ_s^t, ρ_g^t = Respective densities at temperature t °C.

t_s^t, t_g^t = Respective times of flow at temperature t °C.

Thus a constant of calibration $\eta_s^t / \rho_s^t t_s^t$ could be obtained for the Ostwald viscometer and the viscosity of the glycerine solution thereby determined at a desired temperature. In a similar manner, the Institute of Petroleum Viscometers Nos.3 and 4 could be standardised by means of the glycerine solution and the viscosity of the castor oil thereby determined.

Readings were carried out in a mercury toluene thermostatically controlled water tank. Temperature measurements were made on a standardised thermometer and temperature control was within 0.1°C. The measurements necessary for the complete evaluation of the viscosity curve for castor oil were as follows.

(1) Time of flow of 60% sucrose solution in the Ostwald viscometer at 25°C. The solution was prepared by dissolving 60 gm. A.R. sucrose in 40 cc. distilled water. This was filtered and 25 cc. pipetted into

the viscometer from a temperature of 25°C. Several solutions were prepared and a series of readings taken on each solution. Readings on each solution did not vary more than 0.5% and over all solutions more than 1%. This gave the average value

$$t_s^{25°C} = 347.3 \text{ sec.}$$

(2) Density of 60% sucrose solution at 25°C.

The densities for the several solutions were averaged to give

$$\rho_s^{25°C} = 1.2851 \text{ gm./c.c.}$$

(3) Time of flow of glycerine solution in Ostwald viscometer at 25°C.

$$t_g^{25°C} = 1787.6 \text{ sec.}$$

(4) Density of glycerine solution at 25°C.

$$\rho_g^{25°C} = 1.2377 \text{ gm./c.c.}$$

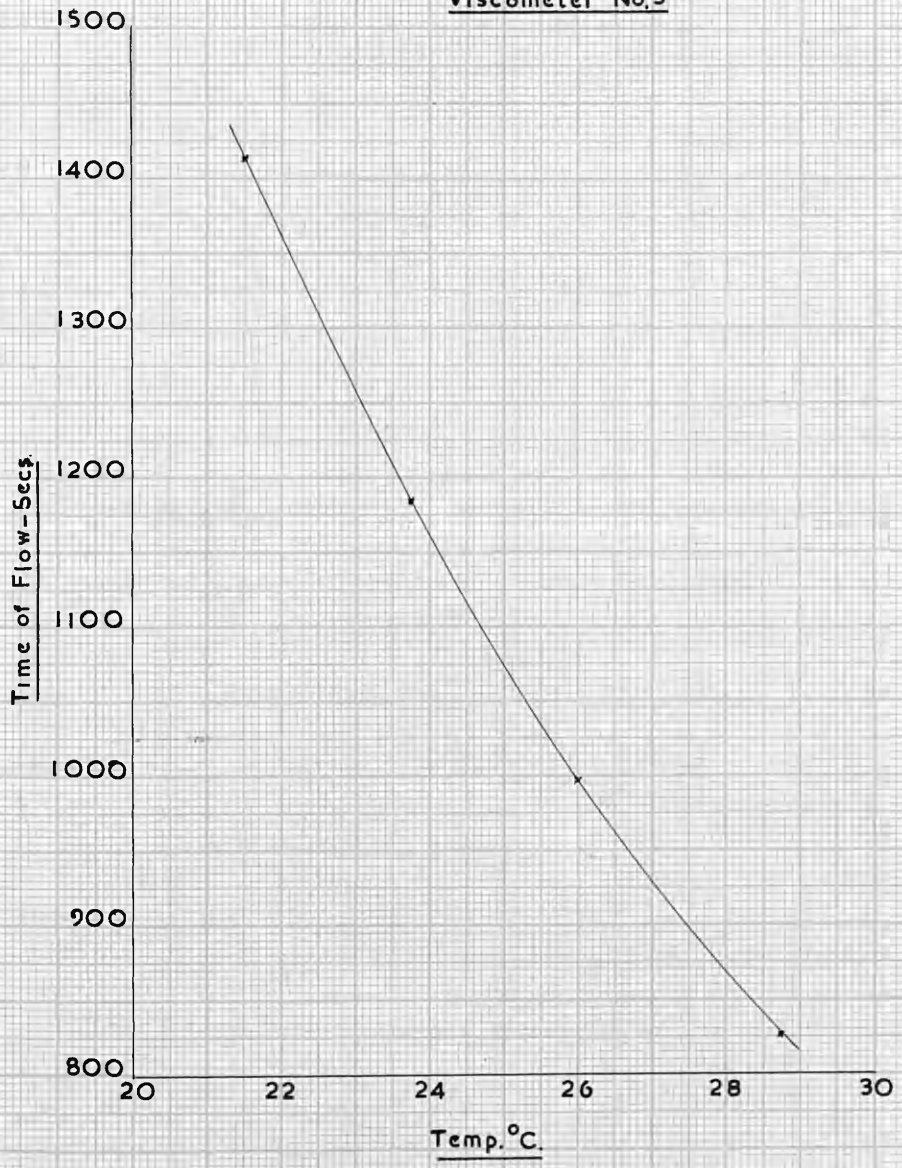
(5) Times of flow of glycerine solution in Viscometers Nos.3 and 4 at 25°C.

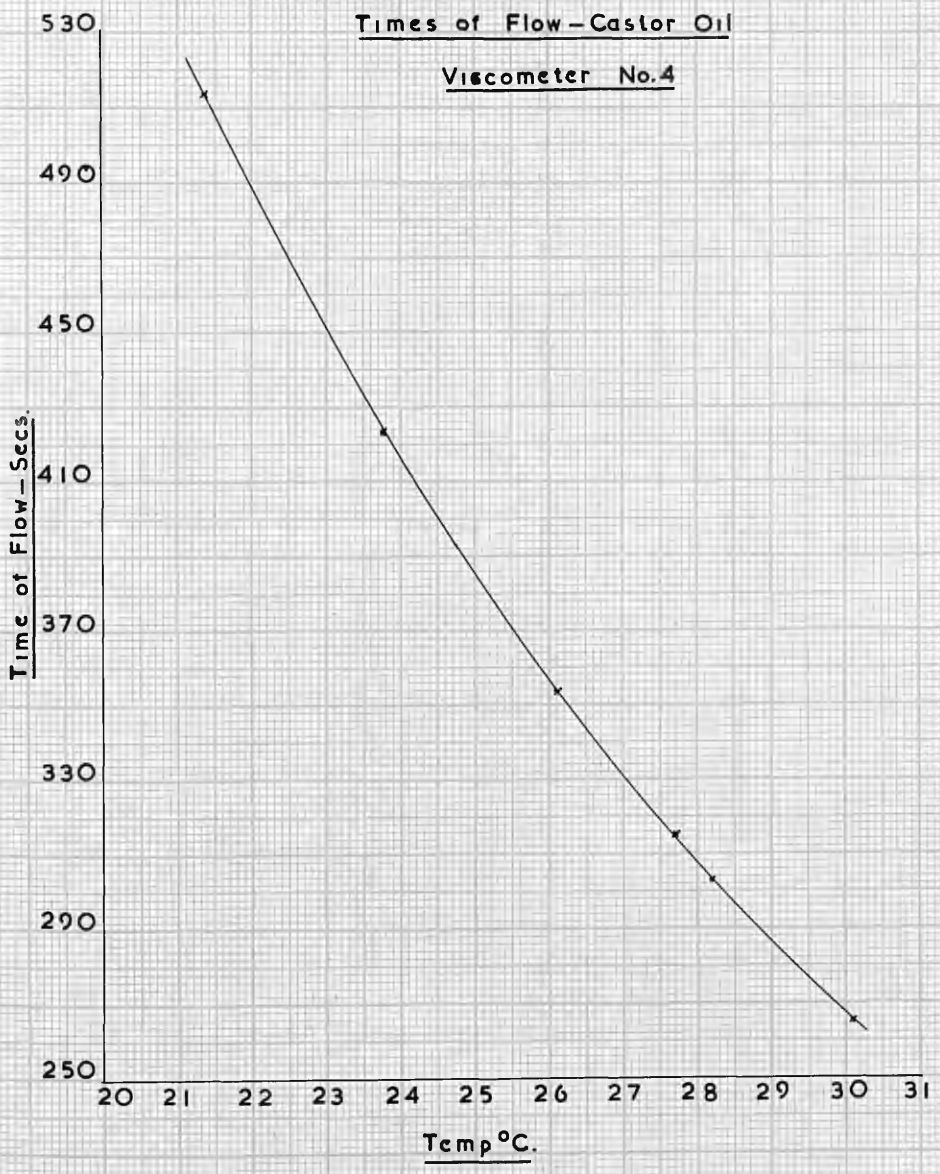
No. 3 = 280 sec. No 4 = 100 sec.

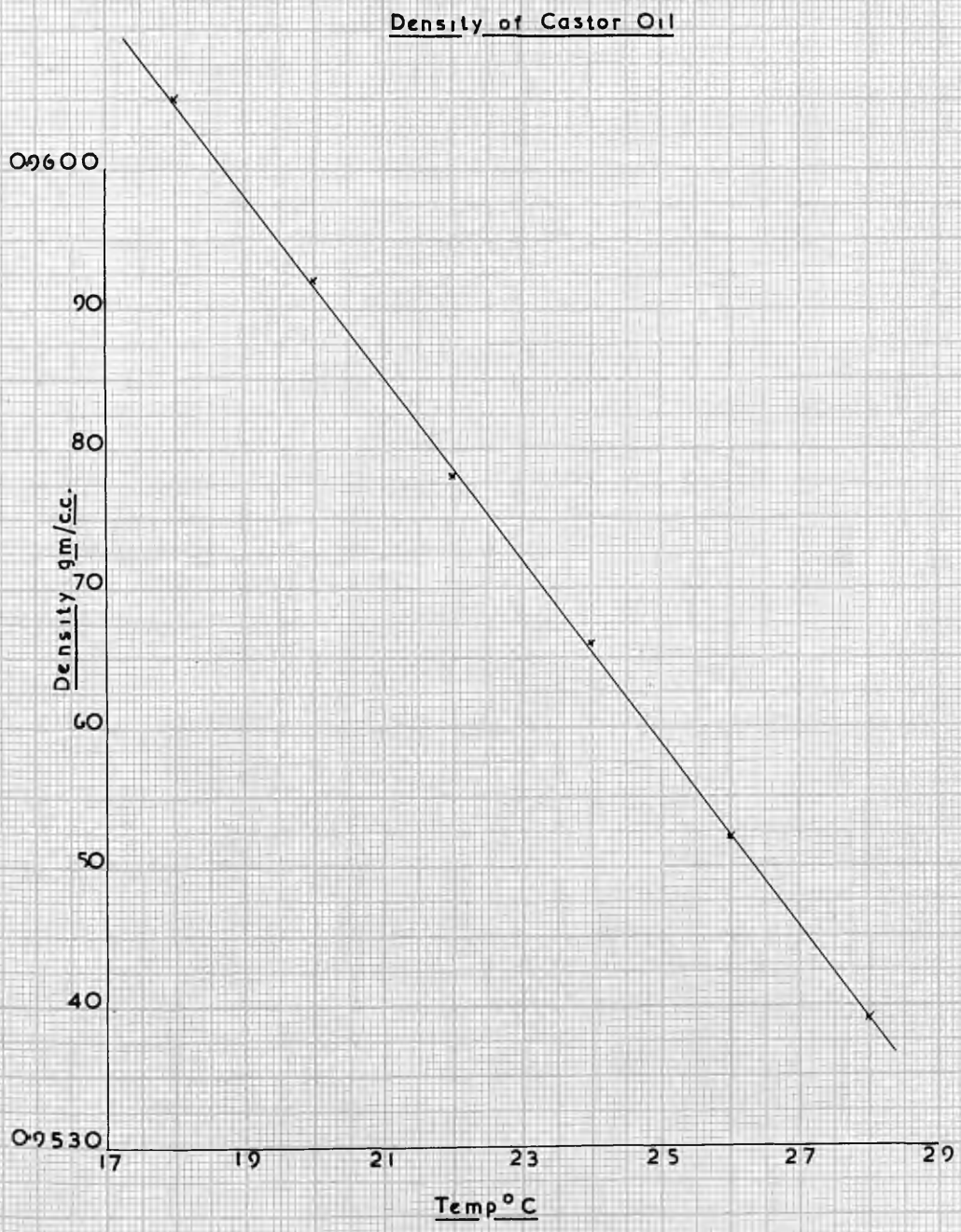
(6) Times of Flow of Castor Oil in No.3 and No.4 over a range of temperature. This is shown in the graphs 1 and 2. The volume of liquid in the viscometer was adjusted at each temperature.

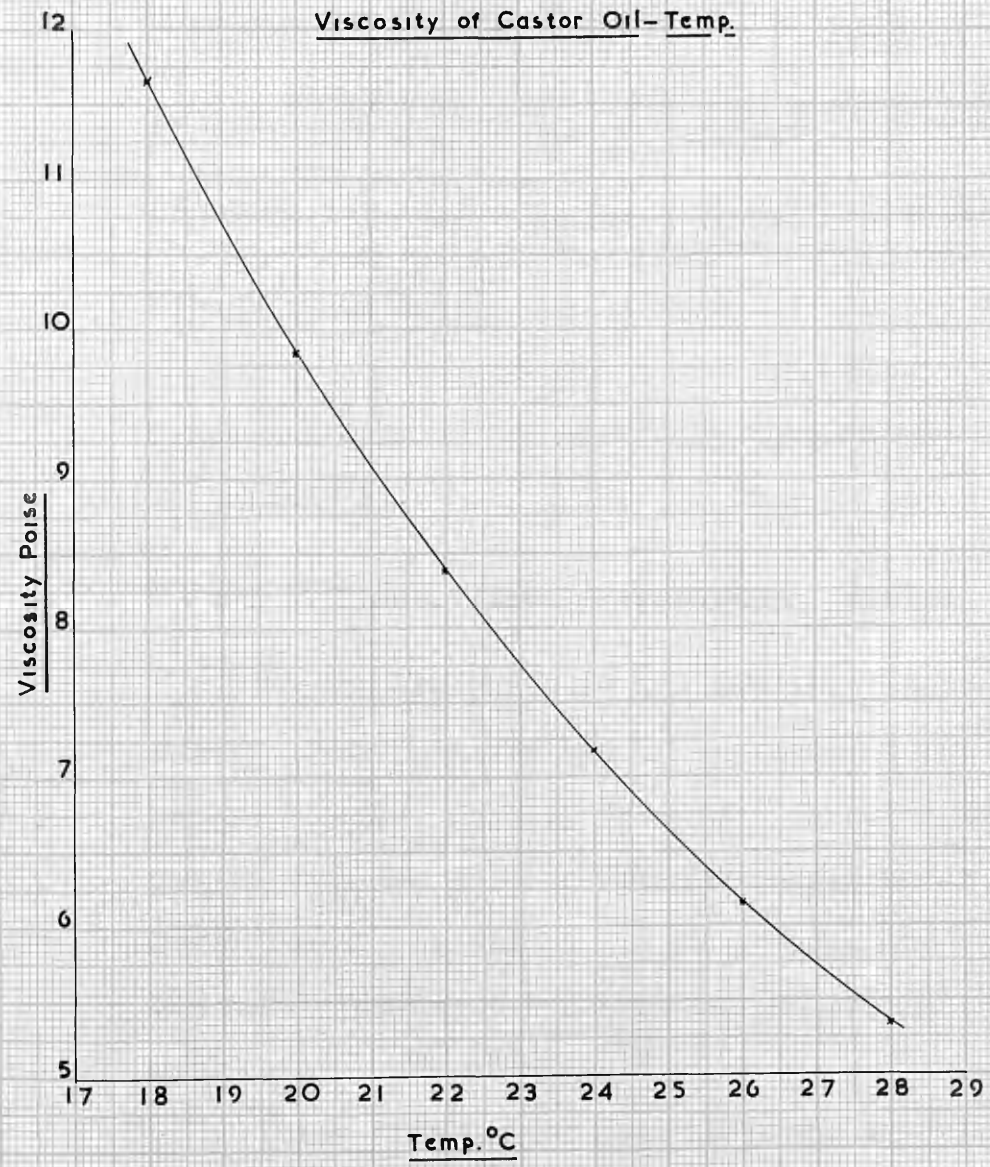
Times of Flow - Castor Oil

Viscometer No. 3




Times of Flow – Castor Oil
Viscometer No. 4
530
490
450
410
370
330
290
250
Time of Flow – Secs.
20
21
22
23
24
25
26
27
28
29
30
31
Temp °C.


Density of Castor Oil
0.9600
90
80
70
60
50
40
0.9530
Density gm/c.c.
17
19
21
23
25
27
29
Temp °C


Viscosity of Castor Oil – Temp.
Viscosity Poise
12
11
10
9
8
7
6
5
17
18
19
20
21
22
23
24
25
26
27
28
29
Temp. °C

(7) Density of Castor Oil over a range of temperature.

This is shown in graph 3.

These measurements gave the following results.

Constant for Ostwald Viscometer $= \frac{\eta_s}{\rho_s t_s} = \frac{0.3511}{347.3}$

Constant for No.3 $= \frac{0.3511}{347.3} \cdot \frac{1787.6}{280} = 0.00645$

Constant for No.4 $= \frac{0.3511}{347.3} \cdot \frac{1787.6}{100} = 0.01807$

Viscosity of Castor Oil at 25°C - by No.3 = 6.63 poise.

by No.4 = 6.65 poise.

Graph 4 indicates the viscosity-temperature relationships for castor oil.

(3) Calibration of Rotating Cylinder System.

For the purposes of calibration, the furnace was removed from position and an arrangement set up as indicated in Fig.4. Through the water jacket A water was pumped from the toluene-mercury regulator at the desired temperature. A slight lag in temperature existed between the regulator and the liquid in the viscometer but very good control was obtained.

Three brass inner cylinders and the platinum cylinder to be used at high temperatures for the slag work, were employed for the calibration with a copper outer cylinder of 1" internal diameter.

Diameter of Inner Cylinders = 0.6356 cm.

Length " " " = 2 cm, 2.68 cm.(Pt)., 3.0 cm. 3.5 cm.

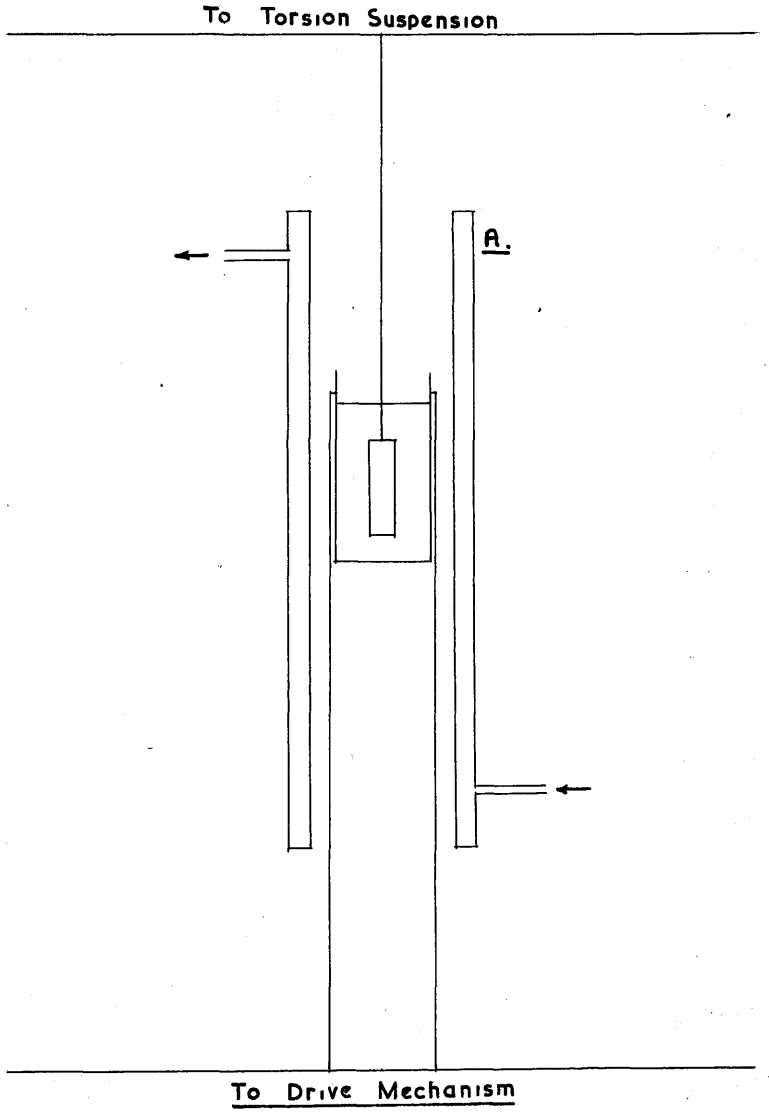


Fig.4

Thus $\eta = \frac{K t \theta}{2\pi C L}$

where $C = 4\pi \frac{R_1^2 R_2^2}{R_2^2 - R_1^2} = 1.356.$

Hence $\eta = \frac{445\, t\theta}{2\pi C L}$ for K_1 i.e., $\eta = 52.25\ t\theta/L$

$= \frac{107.8\, t\theta}{2\pi C L}$ for K_2 i.e., $\eta = 12.66\ t\theta/L$

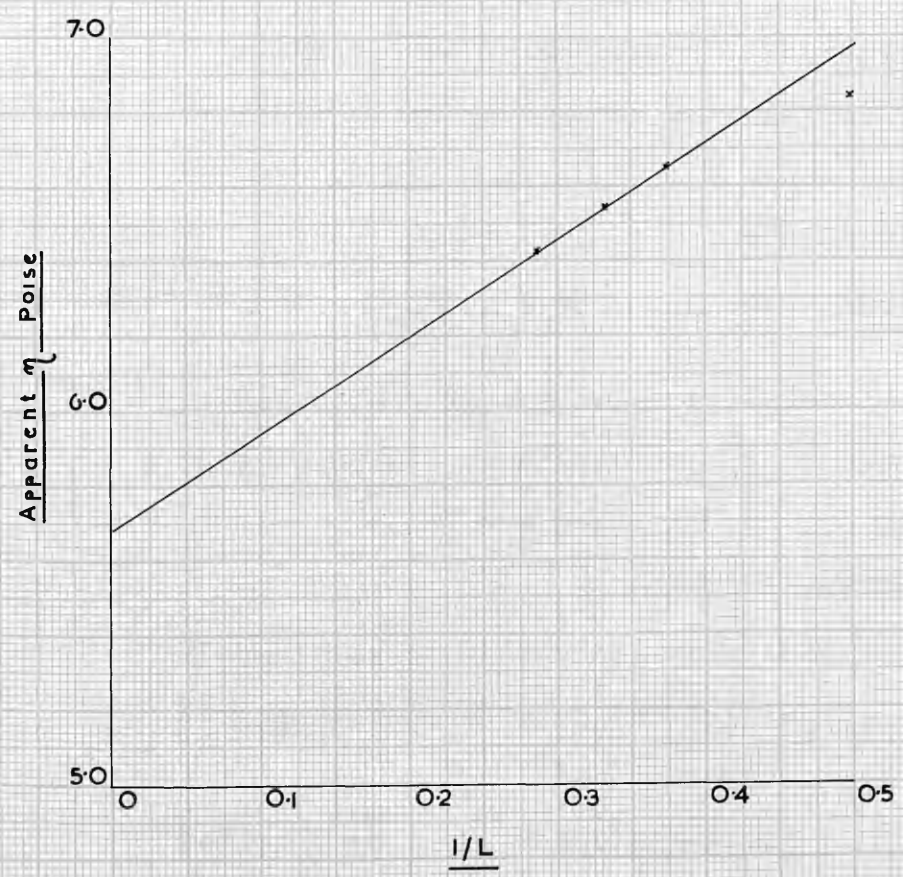
Readings taken at 27.1°C gave the following results and these have been plotted in graph 5.

Torsion Wire	η (Poise). 2 cm.	2.68 cm.	3.0 cm.	3.5 cm.
K_1	6.83	6.64	6.52	6.40
K_2	6.85	6.66	6.56	6.44

In all the readings the end separation was maintained at 0.6 cm. and the liquid stood at 1 cm. above the top of the inner cylinder. When these results are plotted against reciprocal length the true viscosity of the oil is obtained by extrapolation to infinite length. Lillie(54) used the above method for the calibration of a rotating cylinder system. He found, using an exhaustive range of inner cylinders, that the apparent $\eta \sim$ reciprocal length plot was linear for values of Length of Inner Cylinder/(Radius of I.C.) $>$ 22.5. Cylinders of lower value tended to give lower values of apparent viscosity. The values for the cylinders used here are shown below.

3.5 cm.	3 cm.	2.68 cm.	2 cm.
34.7	29.9	25.5	19.8

Apparent η – Reciprocal Length



On the basis of these figures, there is good reason to expect that the 2 cm. cylinder gives a value of apparent η on the non linear portion of the apparent η ~ reciprocal length relationship. A straight line has therefore been drawn through the points for the three longest cylinders only and as can be seen gives a value closely in agreement with the value of 5.70 poise obtained by capillary viscometry.

Using the values for the platinum inner cylinder at 27.1°C the end effect was calculated.

$$\eta = X/L \quad \therefore X = \eta L$$

$$= 6.65 \times 2.68$$

$$\therefore L = \frac{6.65 \times 2.68}{5.70} \qquad = 3.12 \text{ cm.}$$

$\therefore$ End effect in the inner cylinder = 0.44 cm.

This resulted in constants of calibration as follows:

$$\eta = 16.74\ t\theta \qquad \text{for } K_1$$

$$\eta = 4.06\ t\theta \qquad \text{for } K_2$$

Viscosities of Castor Oil were then measured over a range of temperature to give the following results.

Temperature	η Poise. By Rotating Cylinder	η Poise. By Capillary Viscometer
27.1°C.	5.73	5.70
25.2	6.57	6.53
22.5	8.10	8.06
20.0	9.90	9.84
19.0	10.75	10.71

Lillie(54) also examined the constancy of the calibration factor for his rotating cylinder viscometer over a wide range of viscosities. This was done by comparison of results from capillary viscometers and indicated that the calibration factor was constant over the range 5.0/3000 poise examined. This almost completely covers the range of viscosity as met in the present work.

A correction to the constant of calibration must be applied due to expansion of the platinum cylinders up to 1600°C. The changes in dimensions of the cylinders were calculated and resulted in the constants as shown in the following table.

Constants of Calibration at High Temperatures.

Temp.°C.	K_1	K_2
1000°C	16.40	3.97
1200°C	16.30	3.95
1400°C	16.20	3.93
1600°C	16.10	3.91

Errors in the Measurement of Viscosity.

The principal sources of error which arise in the measurement of slag viscosity are considered below. Consideration of these is necessary for complete calibration of the apparatus.

(1) Dimensions of the Cylinders. Room temperature calibration takes no account of the error introduced due to expansion of the cylinders as the temperature is raised. Accordingly the changes in dimensions of the cylinders (platinum) have been calculated up to 1600°C and the calibration factor adjusted for each temperature. This has already been shown.

(2) Alignment of Cylinders. Rait and Hay(32) have shown that misalignment to the extent of 2% of the annular space may introduce an error of 0.5% in the viscosity determination. This degree of misalignment is easily discernable to the eye so that this error can be made very small. Tests at room temperature on the present apparatus with the cylinders in obvious misalignment showed an error of 1%. In practice any misalignment of the cylinders is immediately observable in the reading by a characteristic oscillation about a mean value. In such a case a repeat determination is made after realignment.

(3) End Correction. This has already been considered.

(4) Depth of Immersion. In the present apparatus where the diameter of the platinum connecting rod is much smaller than the diameter of the inner cylinder itself, errors due to changes in the height of liquid above the top of the inner cylinder are negligible. In all cases the crucible was filled with slag to a height of 1 cm. from the top of the crucible in which case the spindle was covered to a depth of 0.8 cm. Errors also arise due to a variation in the end separation of the cylinders. This was always maintained at 0.6 cm.

(5) Speed of Rotation. The error produced in the value of viscosity is proportional to any error in the measure-:ment of the period of revolution. This was always measured accurately with a stop watch.

(6) Temperature Measurement. As in all high temperature work this probably constitutes the greatest single source of error in the value of viscosity obtained. Temperature was measured with a Pt-Pt 13% Rh. thermocouple which was standardised with gold (M.Pt.1063^{o}C) and palladium (M.Pt.1554^{o}C) wires, and was found to conform closely with the given e.m.f. values. The e.m.f. was measured by a Cambridge potentiometer and the thermocouple was restandardised from time to time. In the present work the e.m.f. fell by 0.2 m.v. over the period of research, probably due to the preferential volatilisation of Rhodium.

Reproducibility of Results.

During the course of any one run, the reproducibility of any result is 1%. A repeat determination involving the preparation of a new quantity of slag and the complete reassembly of the apparatus lowers the reproducibility to 2%. Care must be taken in the preparation of the apparatus regarding alignment of cylinders for this reproducibility to be achieved.

Preparation of Materials.

SiO_2 Silica sand was acid washed to an analysis of 99.8% and ground to -200 mesh.

CaO This was obtained by igniting Analar $CaCO_3$ to 900°C for two hours with excess of air. The lime component of any slag was always weighed as car-:bonate.

MgO High purity fused magnesia was used and ground to -200 mesh.

MnO This was prepared by the decomposition of manganese oxalate in an atmosphere of hydrogen at 1000°C. The charge of oxalate was held at 1000°C. for one hour and then allowed to cool to room temperature with hydrogen passing continuously. This yielded a bright green powder of 99.5% purity which was stored in a sealed bottle. Exposure to atmosphere for a considerable time resulted in a diminution in the brilliance of the green colour.

Slag The slag was always premelted in the platinum crucib-:le some time previous to the experimental run. Requisite quantities of the finely ground components were mixed thoroughly in an agate mortar. The platinum crucible was half filled with slag mixture, loaded into the furnace, and the mixture melted. The remainder of the mixture was compressed into pellets of suitable size and additions to the crucible made through an iron tube. Care was

taken to see that the tube never became oxidised. Several of the slags examined were analysed after an experimental run and found to conform with the synthetic composition. In all the investigations here the same technique was rigidly adhered to so that there is no reason to expect deviations in composition from the compositions given.

Manganese containing slags were melted in a controll-:ed atmosphere. A mullite tube projecting 1ft. above the furnace top was fitted and the lower end sealed to the iron plate with water glass (Fig.1B). A gas tight system was thus obtained and melting carried out in nitrogen.

During experiment however, the system is always open to atmosphere via the small hole for the platinum spindle at the brass guides. It was found necessary to have a little hydrogen passing through with the nitrogen in order to avoid oxidation of the manganese silicate slag. This had no apparent harmful effect on the platinum crucible or on the thermocouple.

One experiment however on a silica saturated slag 80% $MnO.SiO_2$ 20% $CaO.SiO_2$ was made with 50% H_2 and 50% N_2. This resulted in the platinum rod breaking off at the slag surface. This appears to be due to the combined effect of H_2 and SiO_2 on platinum which is known to have a deleterious effect due to the formation of a platinum silicide.

Procedure.

For reproducible results to be obtained the viscometer had to be prepared carefully with respect to crucible alignment. The platinum crucible is held in an alundum cup which is then positioned on top of the alundum spindle. (Fig. 1A).

Any free space between the platinum crucible and the sides of the alundum cup is taken up with fired alundum powder so that no shifting in position of the crucible could occur.during rotation. The alundum cup was prepared by casting a slip into a mold of desired shape, drying and then filing to the correct size. It was then fired in a carbon crucible to 1500°C by high frequency induction heating. No spalling occurred during heating.

With the furnace in the raised position, a plumb line was suspended from the centring device and the alundum spindle adjusted until the platinum crucible rotated concentrically. The furnace was lowered and the water cooled top clamped in position. The plumb line was removed and the suspension system set up. With the temperature controller set at 1400°C the furnace was allowed to heat overnight and raised to 1600°C in the morning The inner cylinder was then lowered into the slag so that the end clearance was 0.6 cm. A period of 15 mn. was generally allowed for the slag to reach

thermal equilibrium before any readings were taken. Thereafter only a few minutes were required before readings could be taken at any particular temperature once the temperature had steadied. If solid were separating however, a longer time was given for the slag to come to equilibrium. In the present work the majority of slags supercooled without any primary crystallisation. In some cases solidification occurred instantaneously at some temperature well below the solidus and in other instances the slag cooled to a glass.

At any one temperature readings were taken at various rates of shear and the period of revolution taken. Readings were taken from 1610°C downwards at small temper-:ature intervals until solidification occurred or until the viscosity of the melt rose outwith the range of the apparatus. Any erratic behaviour in the rotation of the crucible was immediately observed in the reading. In these instances the results were discarded. The separation of primary silica in silica saturated slags made it impossible in many instances to obtain a reading. This was so when the degree of separation was considerable but small amounts did not interfere with the reading. The silica which separates in the manganese silicate slags floats to the surface, rather than remaining dispersed throughout the liquid. This is of course due to the difference in density between the silica and the remaining

manganese silicate liquid.

As the viscosity of the slag rose to very high values in the supercooled state it was found that the temperature control was not fine enough to give a constant reading. This is due to the very high temper-:ature coefficient of viscosity of the liquid in the highly supercooled state. Thus a variation of 5 centigrade degrees during the on-off action of the electronic controller was accompanied by a considerable change in viscosity. The reading on the viscometer could be seen to follow the recorded temperature of the slag as this oscillated about a mean temperature due to the operation of the controller. In this case, the viscosity reading was taken as the needle of the potentiometer, recording the temperature of the slag, crossed the zero position. The accuracy of the viscosity values for the highly supercooled melts must however be considered slightly lower than for higher temperature determinations.

P A R T 5.

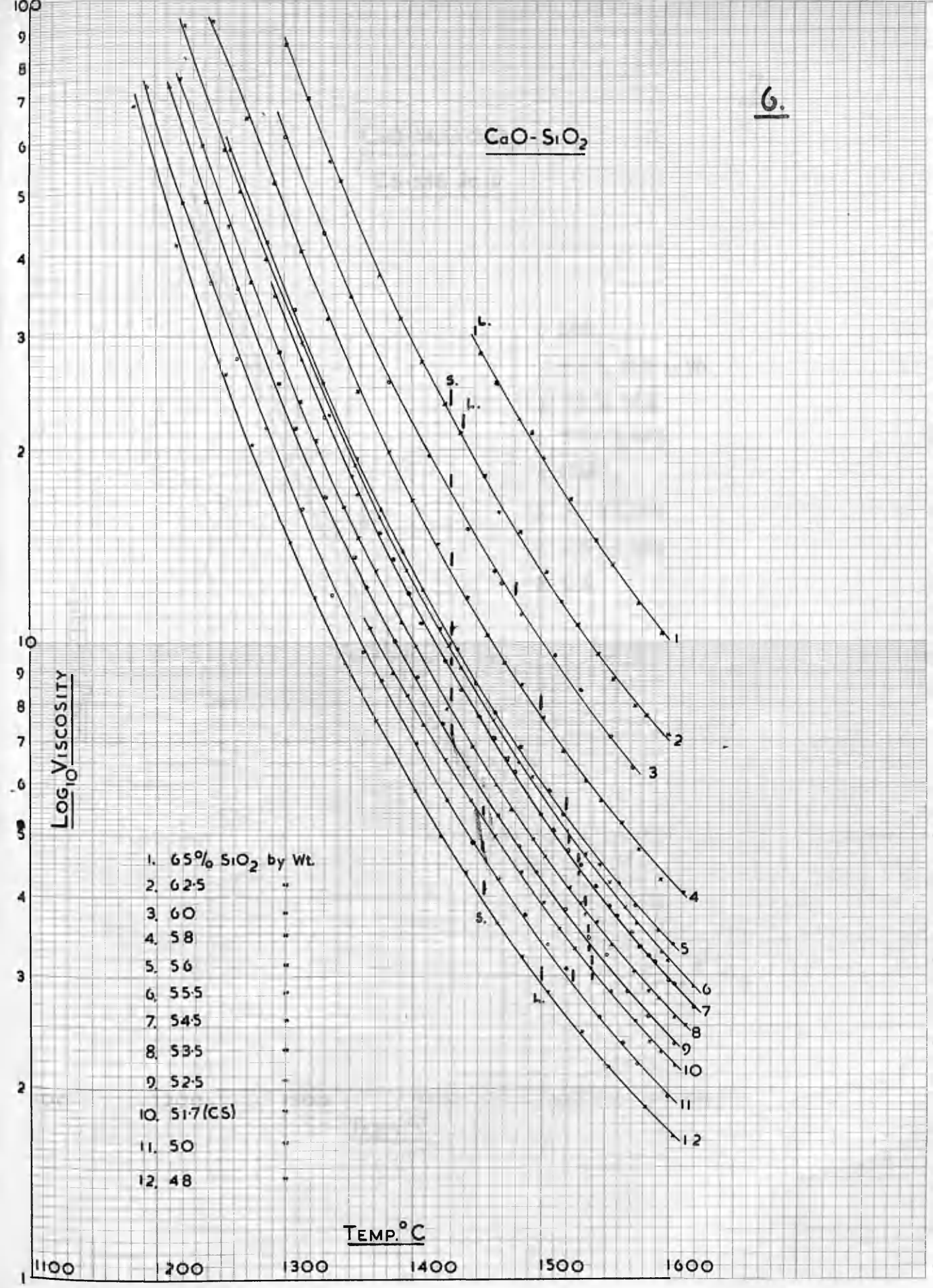
RESULTS AND DISCUSSION OF RESULTS.

SECTION 1. CHANGE OF VISCOSITY WITH TEMPERATURE.

The range of viscosity covered in the examination of these slags was very extensive and so results have been plotted for each series $CaO-SiO_2$; $CaO-MgO-SiO_2$; $CaO-MnO-SiO_2$ on a log η ~ temperature basis. In this way almost the full range of viscosity has been shown in one graph. However, a curve of viscosity - temperature is also given for each slag (graphs 9,10,11,12) over the high temperature range 1400°C - 1600°C. and tables of viscosity are provided in the appendix for the purposes of reference.

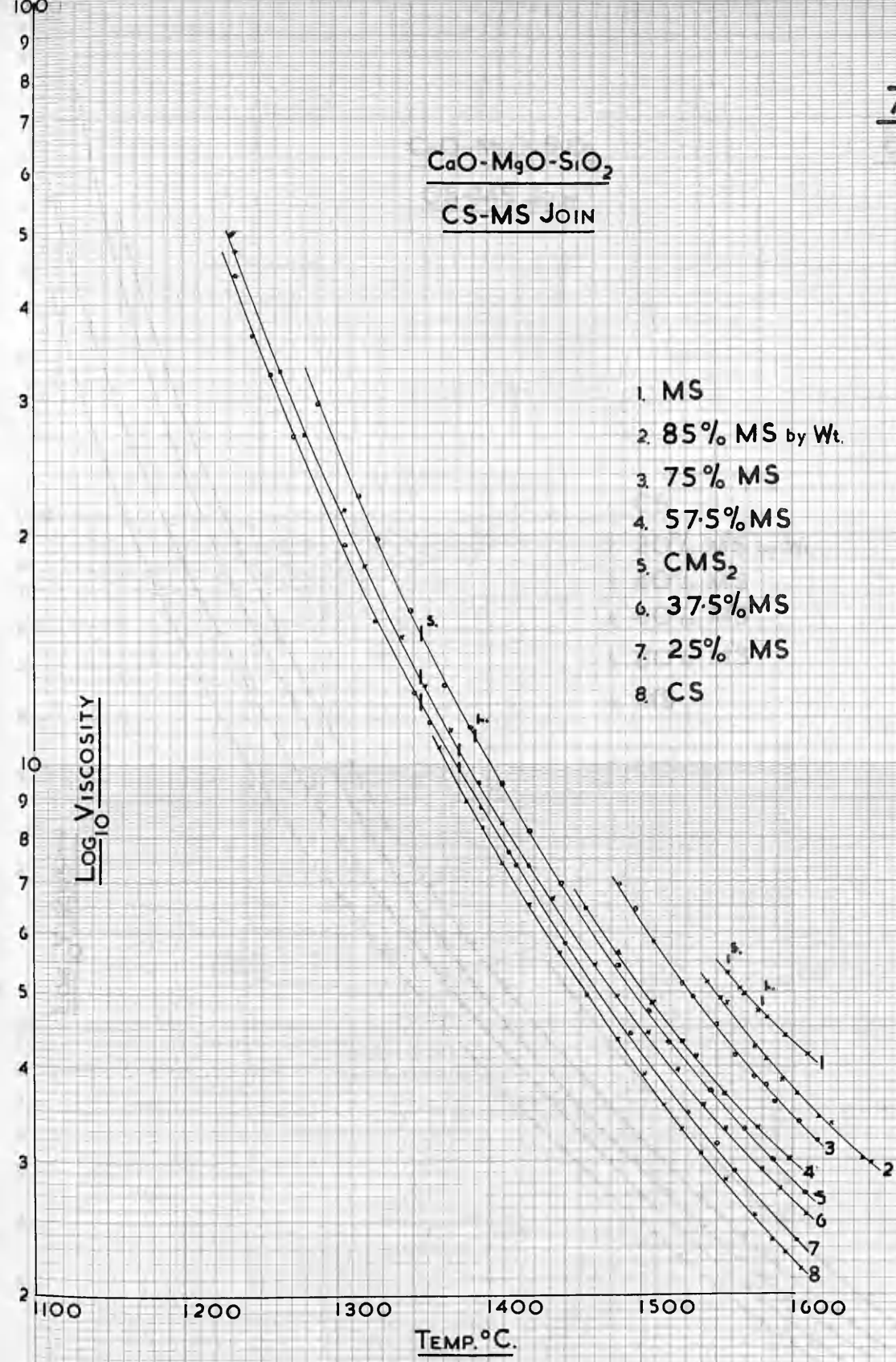
The thermal equilibrium diagrams for each binary system are shown and also the ternary $CaO-MgO-SiO_2$. The published binary joins $CaO.SiO_2-CaO.MgO.2SiO_2$ and $CaO.SiO_2-MnO.SiO_2$ are also shown. The published diagrams(55) of the $CaO.SiO_2-MnO.SiO_2$ join are not compatible with the published binary $MnO-SiO_2$(55) diagram since the former indicate the liquidus temperature for $MnO.SiO_2$ to be 1208°C while the latter indicates 1450°C. In the present work it has been found that separation of silica begins at 1540°C.

Reference to graph 6 showing the log η ~ temper-:ature relationship for the $CaO-SiO_2$ system indicates the degree of supercooling which has occurred for these slags. Liquidus and solidus temperatures are indicated. The least degree of supercooling is shown by the compound $Cao.SiO_2$ and by the slag 65% SiO_2 35% CaO. In the


CaO-SiO2
Log10 Viscosity
Temp. °C
1100
1200
1300
1400
1500
1600
1. 65% SiO2 by Wt.
2. 62·5 "
3. 60 "
4. 58 "
5. 56 "
6. 55·5 "
7. 54·5 "
8. 53·5 "
9. 52·5 "
10. 51·7 (CS) "
11. 50 "
12. 48 "
L.
S.

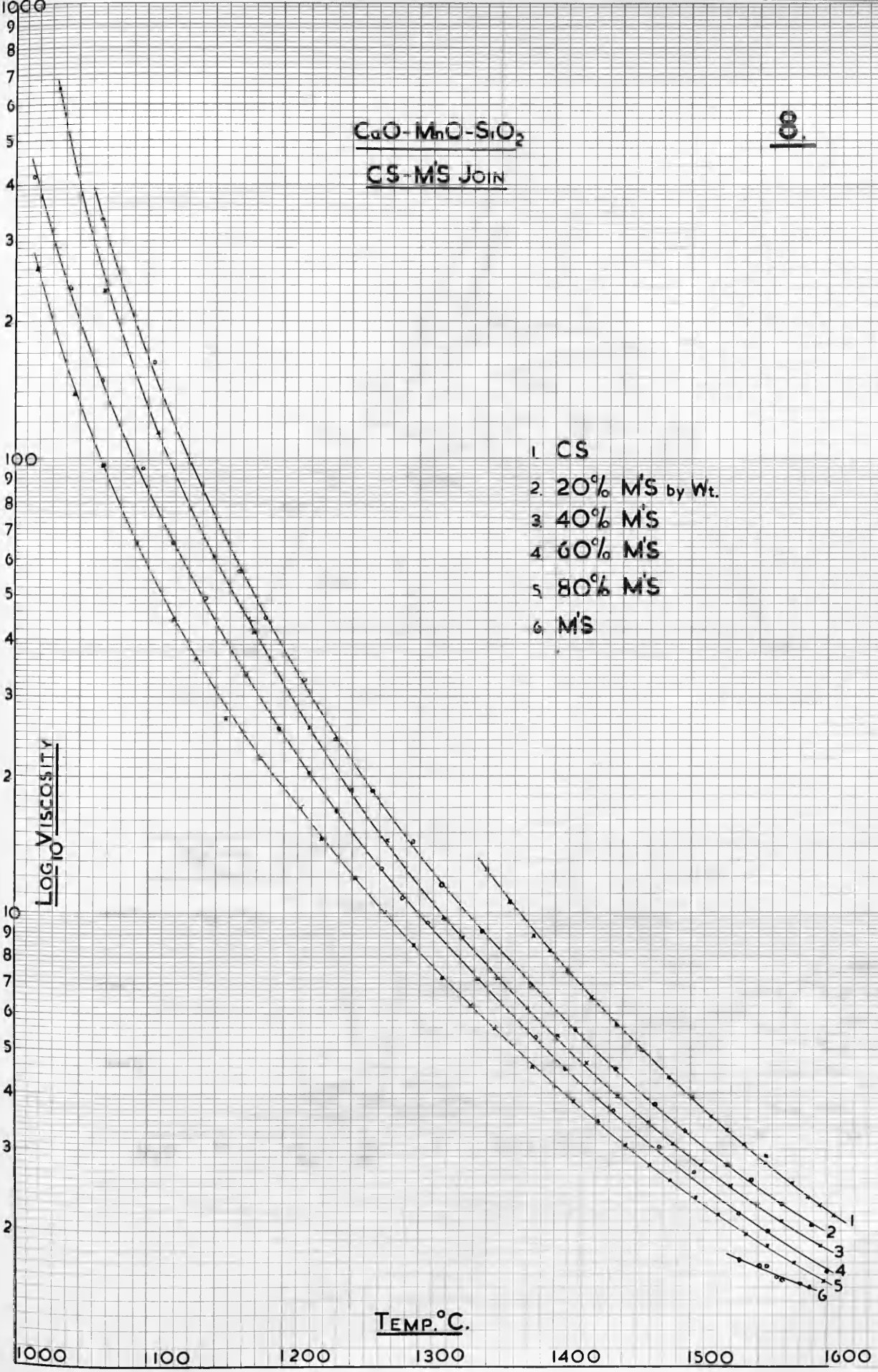
$CaO-MgO-SiO_2$

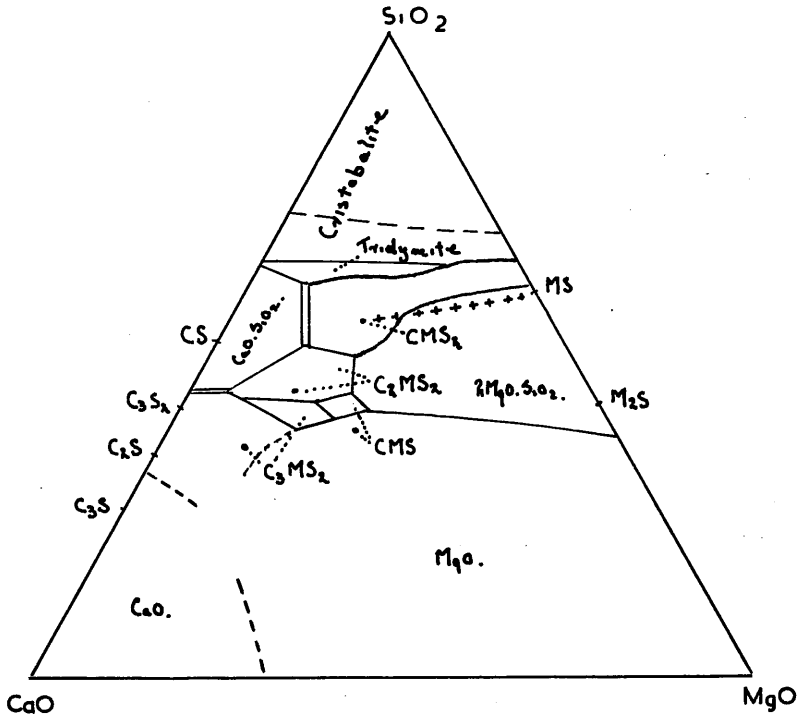
CS-MS Join

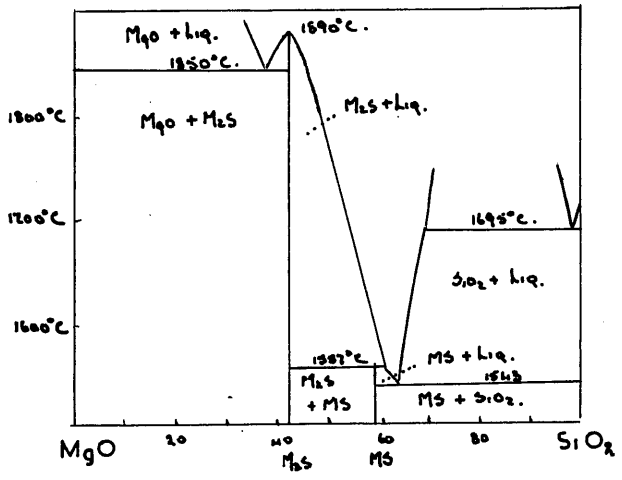


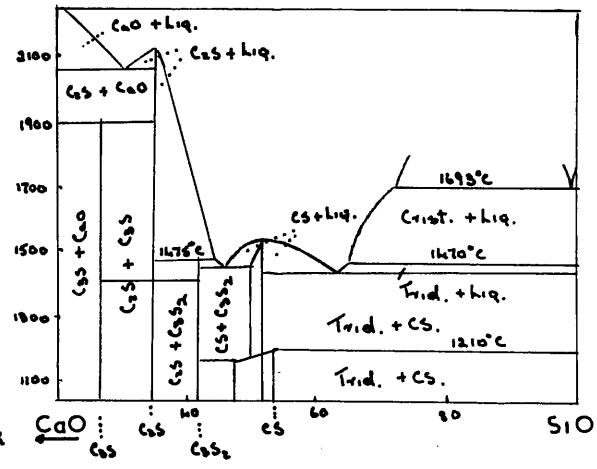
$CaO-MnO-SiO_2$

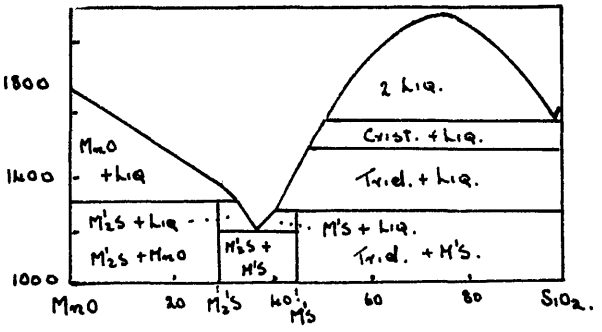
CS-M'S Join

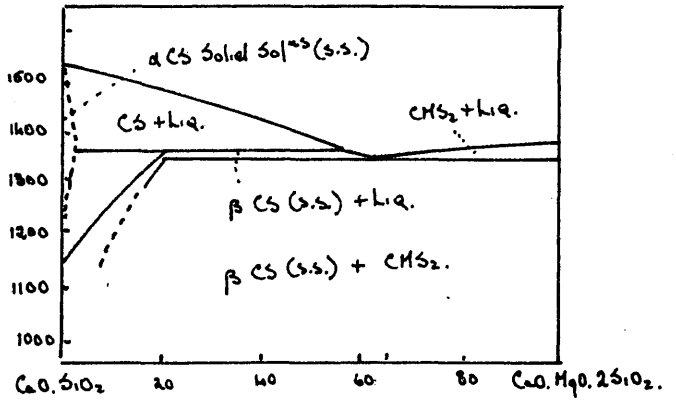


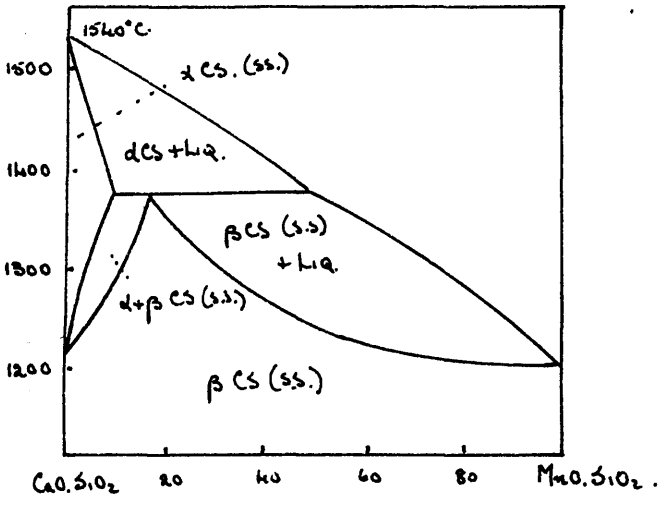

SiO2
Cristobalite
Tridymite
MS
CS
CaO.SiO2
CMS2
C2MS2
2MgO.SiO2.
M2S
C3S2
C2S
CMS
C3MS2
C3S
MgO.
CaO.
CaO
MgO


MgO + Liq.
1690°C.
1850°C.
1800°C
M2S + Liq.
MgO + M2S
1700°C
1695°C.
SiO2 + Liq.
1600°C
1557°C
MS + Liq.
M2S + MS
1543
MS + SiO2.
MgO
20
40
60
80
SiO2
M2S
MS

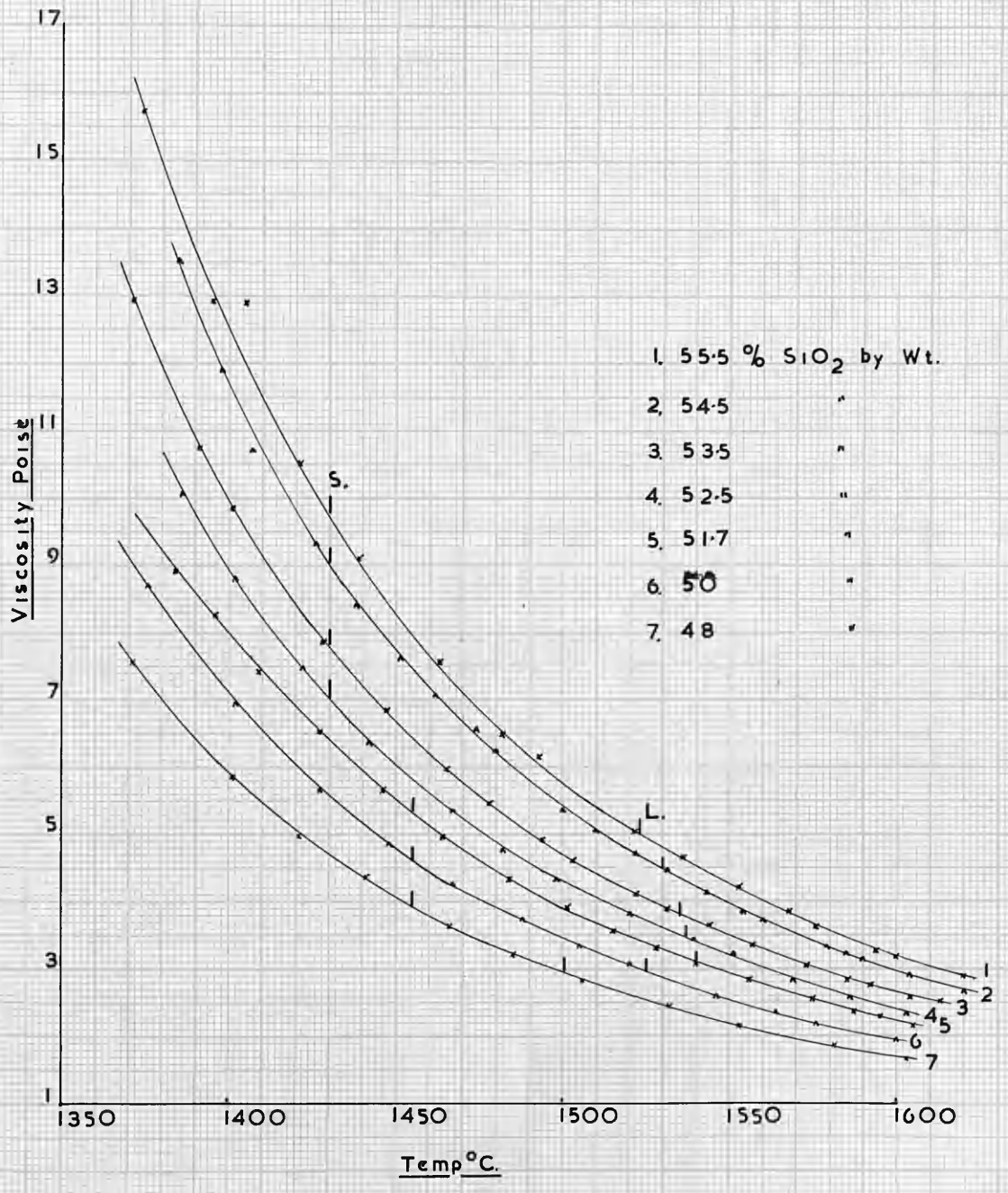

CaO + Liq.
2100
C2S + Liq.
C2S + CaO
1900
1700
1695°C
CS + Liq.
Cryst. + Liq.
1500
1475°C
1470°C
Trid. + Liq.
1300
Trid. + CS.
1210°C
1100
Trid. + CS.
CaO
20
40
60
80
SiO2
C3S
C2S
C3S2
CS


1800
1400
1000
MnO
+Liq
2 Liq.
Crist. + Liq.
Trid. + Liq.
M'2S + Liq
M'2S + MnO
M'2S + M'S
M'S + Liq.
Trid. + M'S.
MnO
20
M'2S
40
M'S
60
80
SiO2.

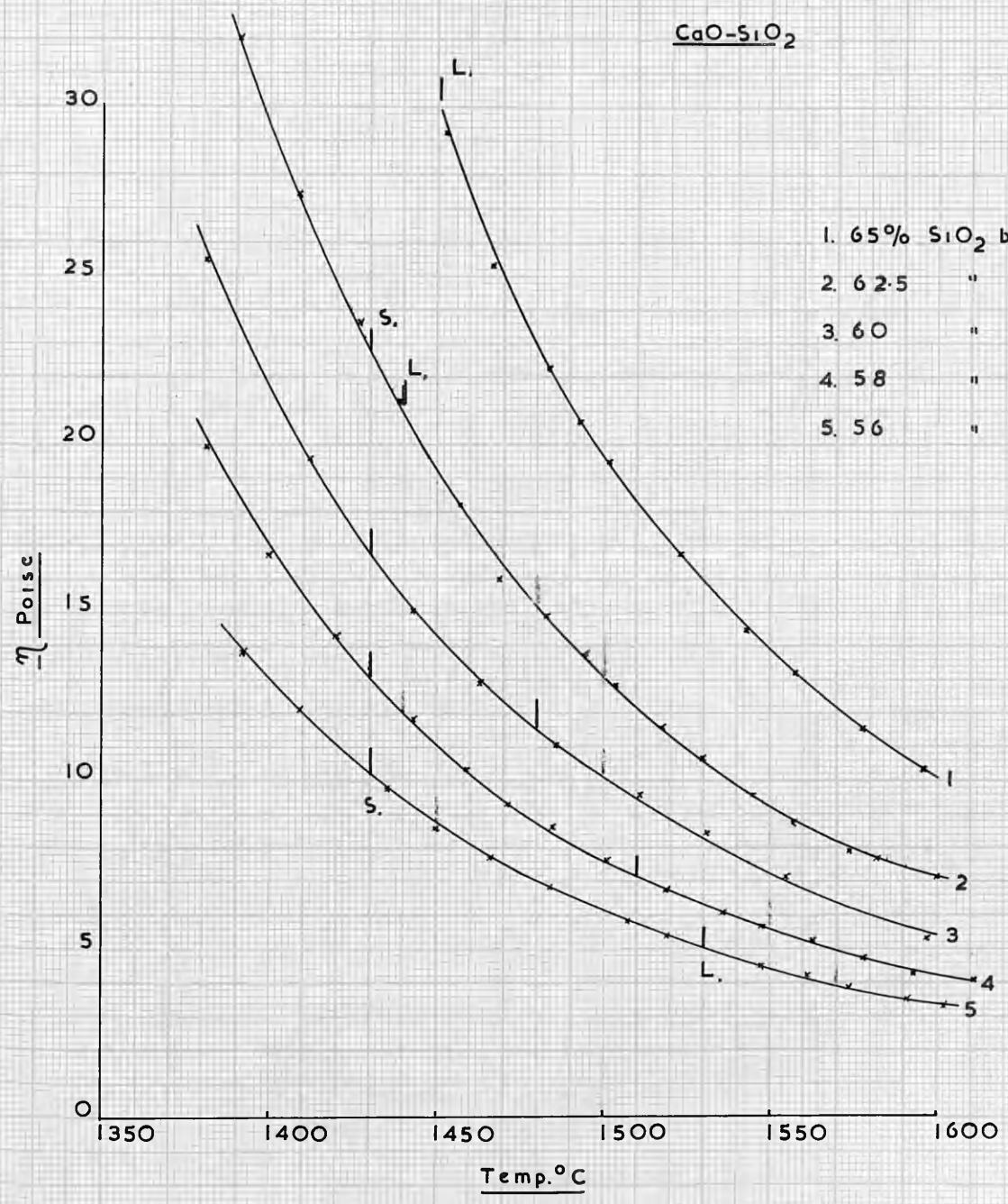

α CS Solid Sol (s.s.)
1600
1400
1300
1200
1100
1000
CS + Liq.
CMS2 + Liq.
β CS (s.s.) + Liq.
β CS (s.s.) + CMS2.
CaO.SiO2
20
40
60
80
CaO.MgO.2SiO2.

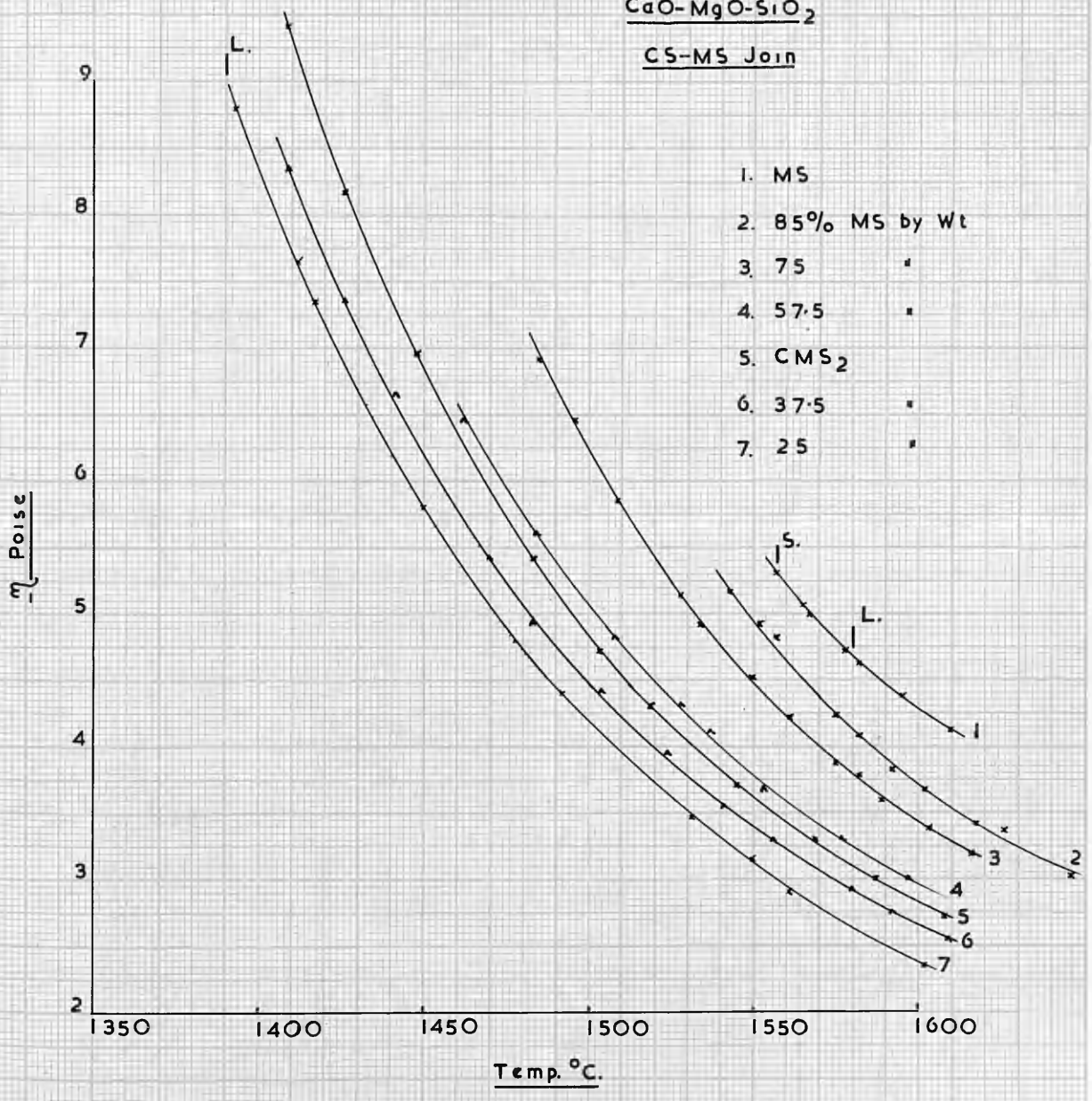

1540°C.
1500
1400
1300
1200
α CS. (ss.)
α CS + Liq.
β CS (s.s)
+ Liq.
α+β CS (s.s.)
β CS (ss.)
CaO.SiO2
20
40
60
80
MnO.SiO2.

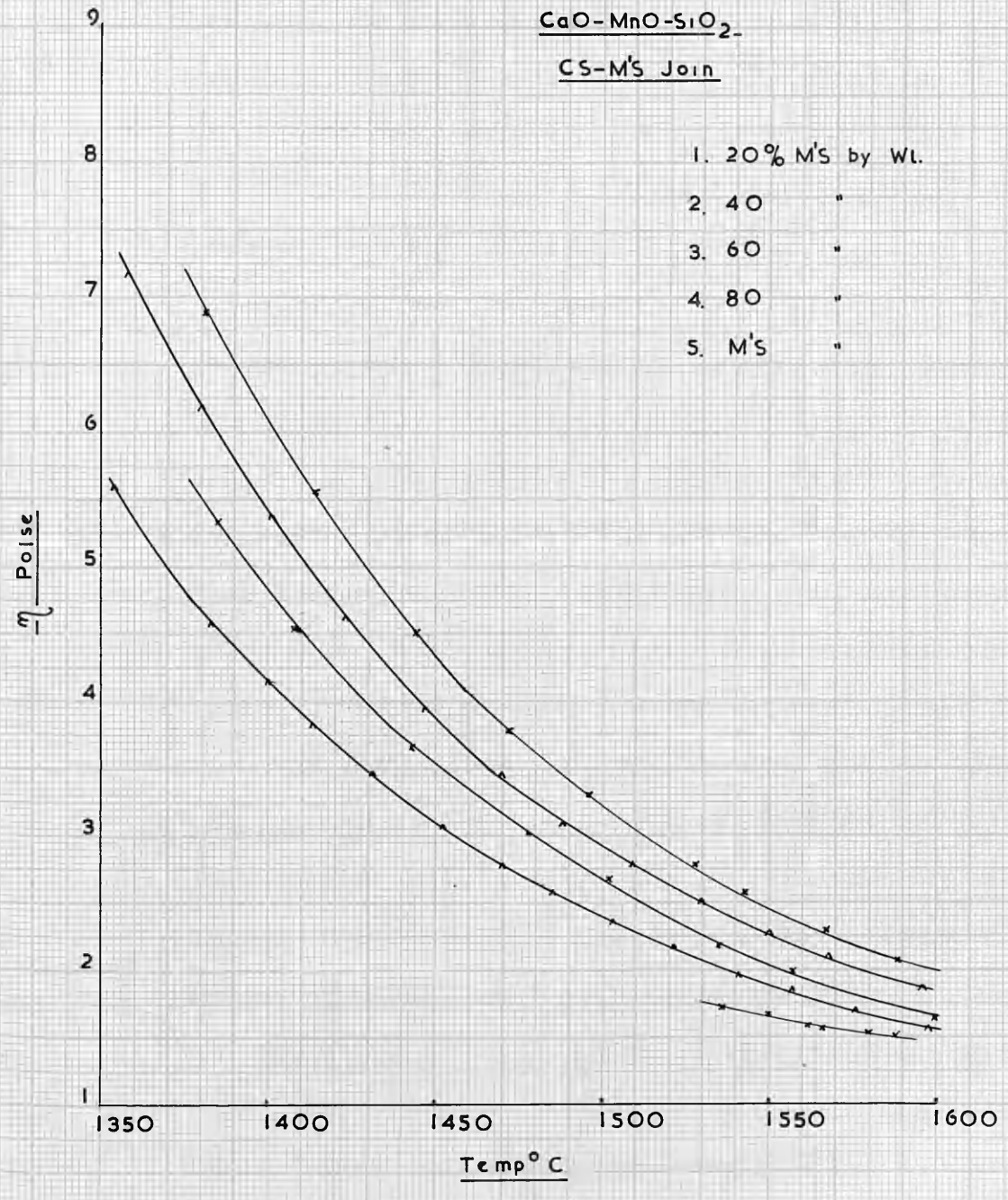
CaO-SiO_2-


Viscosity Poise
17
15
13
11
9
7
5
3
1
1350
1400
1450
1500
1550
1600
Temp °C.
S.
L.
1. 55·5 % SiO_2 by Wt.
2. 54·5 "
3. 53·5 "
4. 52·5 "
5. 51·7 "
6. 50 "
7. 48 "
1
2
3
4
5
6
7

10.


CaO-SiO2
1. 65% SiO2 by Wt.
2. 62·5 "
3. 60 "
4. 58 "
5. 56 "
L.
S.
L.
S.
L.
1
2
3
4
5
η Poise
0
5
10
15
20
25
30
1350
1400
1450
1500
1550
1600
Temp.°C


CaO-MgO-SiO2
CS-MS Join
1. MS
2. 85% MS by Wt
3. 75 "
4. 57·5 "
5. CMS2
6. 37·5 "
7. 25 "
L.
S.
L.
1
2
3
4
5
6
7
9
8
7
6
5
4
3
2
η Poise
1350
1400
1450
1500
1550
1600
Temp. °C.


CaO-MnO-SiO2-
CS-M'S Join
1. 20% M'S by Wt.
2. 40 "
3. 60 "
4. 80 "
5. M'S "
η Poise
9
8
7
6
5
4
3
2
1
1350
1400
1450
1500
1550
1600
Temp° C

former case although considerable supercooling did occur (liquidus temperature 1540°C) the slag always crystallised between 1300°C and 1350°C. and this behaviour has been observed in each of the slag series, i.e., in general supercooling is least at compound compositions. In the 65% SiO_2 slag no readings were possible below 1450°C due to the separation of silica. This is in accordance with the thermal equilibrium diagram.

Of the other slags readings on the 60% SiO_2 composition had to be stopped dueto a broken thermocouple. The 54.5% SiO_2 slag crystallised at 1280°C and the 56% SiO_2 at 1240°C. All other slags cooled to temperatures considerably lower than this before crystallising. At room temperature they consisted of a milky white material. The range of viscosity for these lime sili-:cates is approximately 2.0 poise to 100 poise.

In graph 7 can be seen the log η ~ temperature relationship for CaO-MgO-SiO_2 slags. In this series supercooling was considerable and the slag 25% MgO.SiO_2 cooled completely to a glass. Beyond diopside CaO.MgO.$2SiO_2$ the degree of supercooling decreased rapidly to a minimum at MgO.SiO_2. These latter slags always showed well developed crystals and would not supercool. Hence only a short range of investigation was possible for these slags. The viscosity values range from approximately 2.0 poise to 30 poise.

Results for the CaO-MnO-SiO_2 system are shown in graph 8. Compositions between the two compounds CaO.SiO_2 and MnO.SiO_2 showed very extensive supercooling. Viscosity measurements on MnO.SiO_2 was restricted in range due tothe precipitation of silica beginning at 1540°C. This liquidus temperature is considerably higher than that indicated (1450°C) in the published MnO.SiO_2 diagram. This composition never cooled without crystallisation beginning below the temperature indicated. In between these compositions the range of viscosity was very extensive ranging from 1.0 poise to $\geq$ 1000 poise. The compositions 60/40 and 40/60 cooled to glasses a deep pink in colour.

The energy of activation for viscous flow (E_η) for each of the slags examined has been calculated from the plot log $\eta \sim 1/T$. The observed slopes are shown in graphs 13,14,15 and 16 in which the log $\eta \sim 1/T$ relationship has been plotted at the highest temperatures in order to obtain E_η. These slags show a non-linear log $\eta \sim 1/T$ relationship when considered over the full range of observed viscosity, and this is shown in graphs 17,18 and 19. In the lime-silica system E_η has been obtained on the points above the liquidus only and in the other systems on the straight portion at the highest temperatures. This latter procedure is followed because the lime-magnesia silica slags showed a definite variation in slope above the liquidus and in the

CaO-SiO$_2$

1. 55.5 % SiO$_2$ by Wt.
2. 54.5
3. 53.5
4. 52.5
5. 51.7
6. 50
7. 48

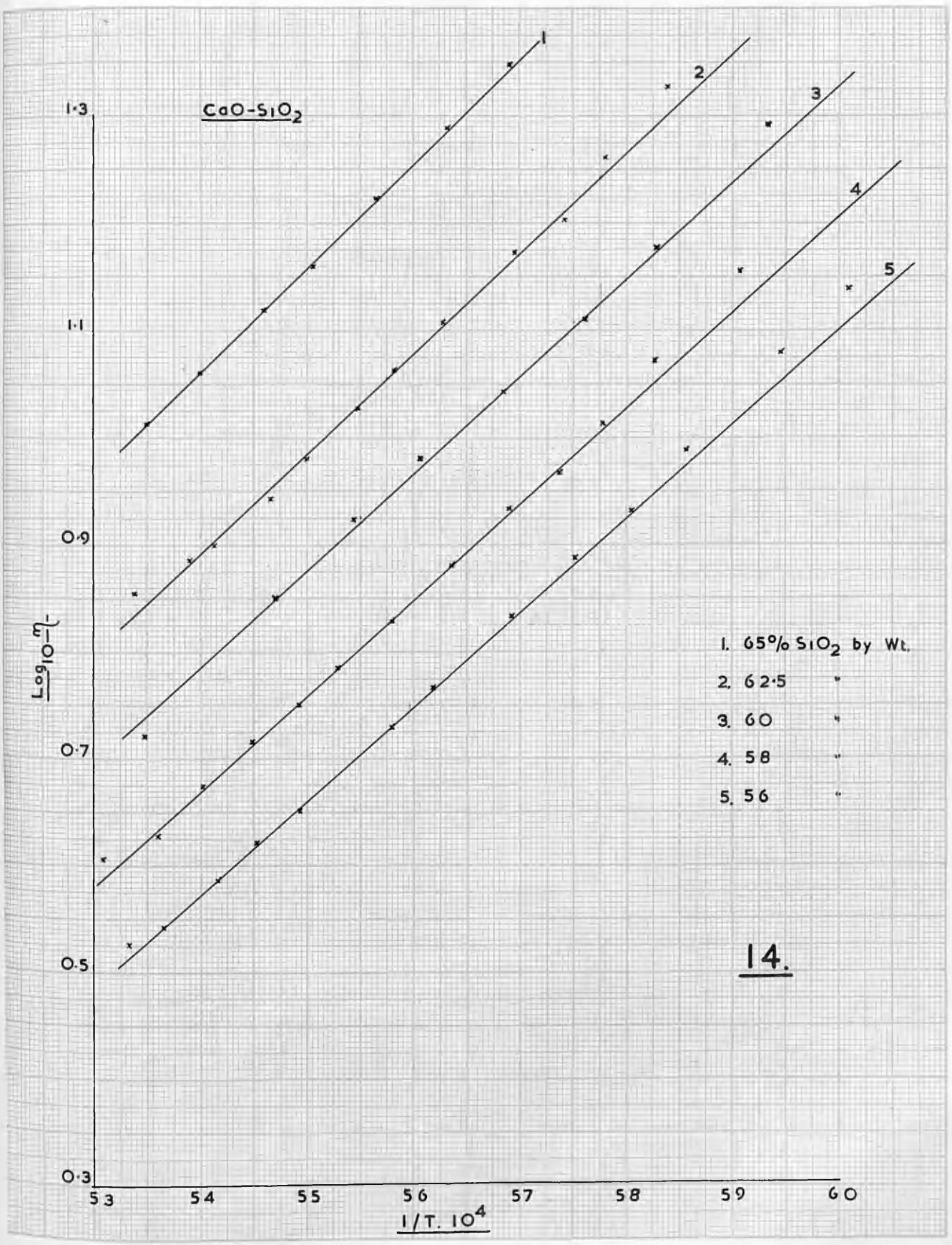
$\log_{10}\eta$

0.8
0.6
0.4
0.2

1
2
3
4
5
6
7

53
54
55
56

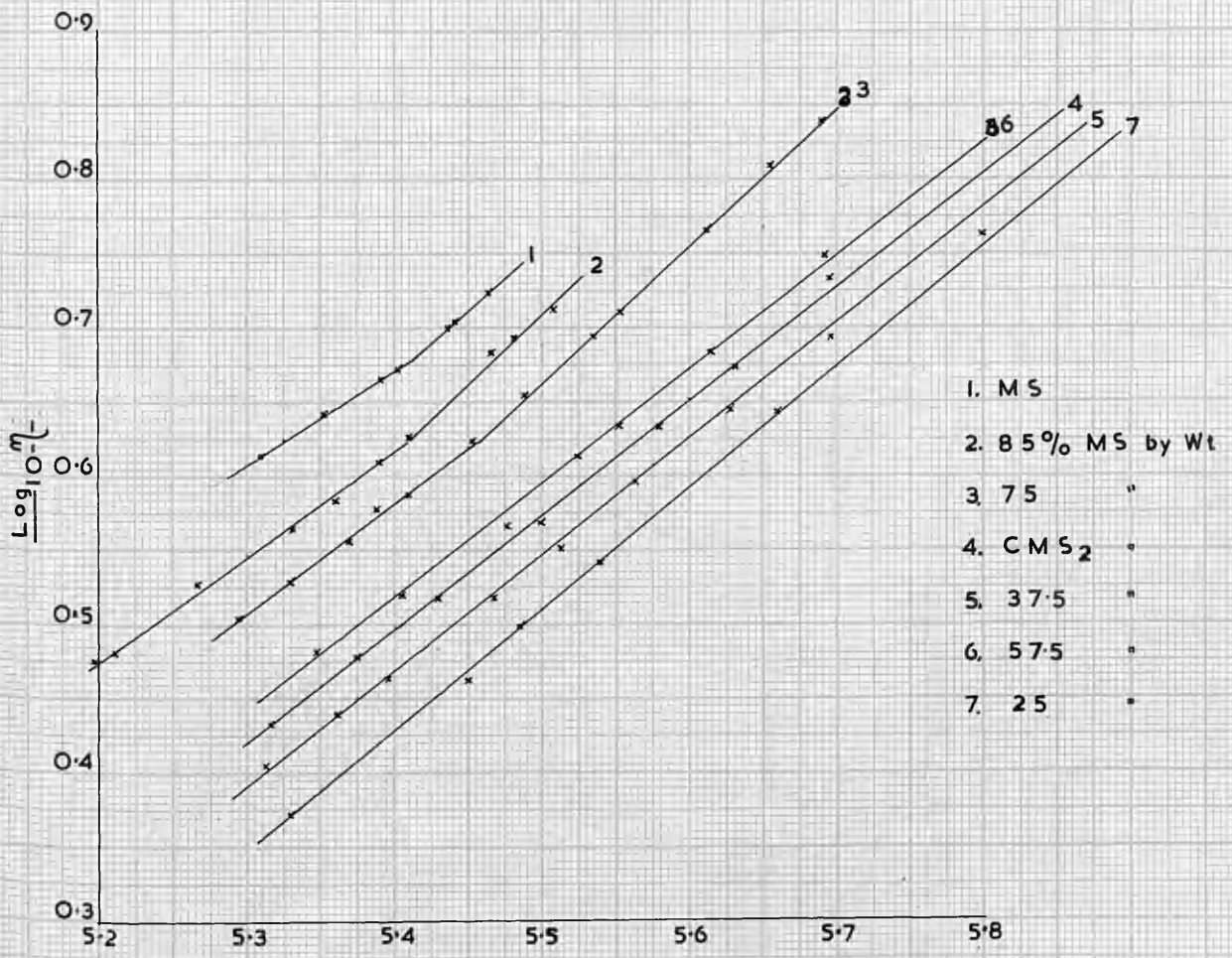
$1/T \cdot 10^4$


CaO-SiO2
1
2
3
4
5
1. 65% SiO2 by Wt.
2. 62·5 "
3. 60 "
4. 58 "
5. 56 "
1·3
1·1
0·9
0·7
0·5
0·3
Log10 η
53
54
55
56
57
58
59
60
1/T. 10^4

14.

$CaO-MgO-SiO_2$

CS-MS Join



$CaO-MnO-SiO_2$

CS–M'S Join

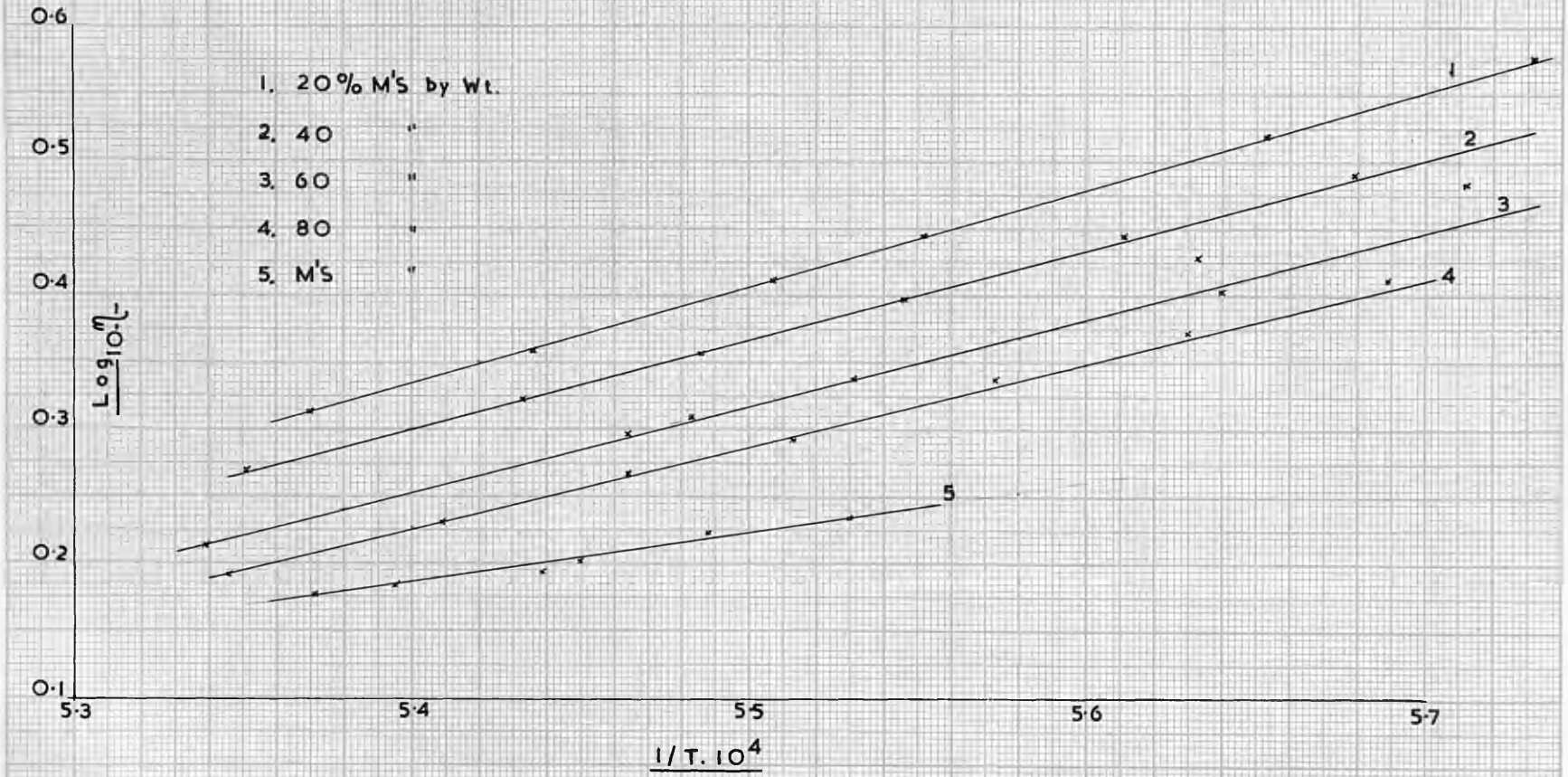
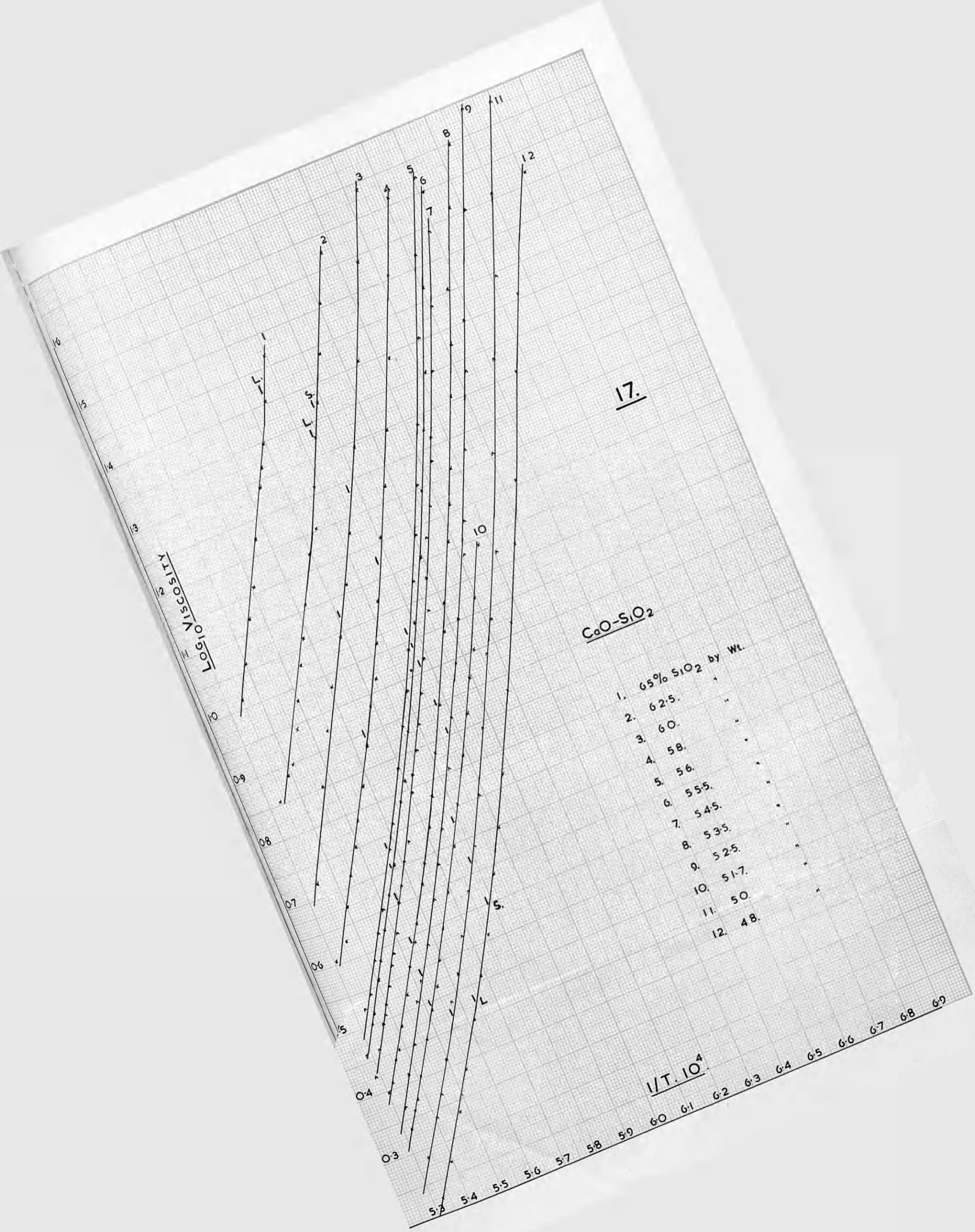


TABLE 1.

Lime-Silica System	Compt. Wt.% SiO_2	E_1 k.cals/mol.
	48	35.8
	50	36.7
	51.7	36.7
	52.5	37.7
	53,5	37.4
	54.5	38.1
	55.5	39.2
	56.0	39.4
	58.0	39.8
	60.0	41.8
	62.5	43.1
	65.0	44.4

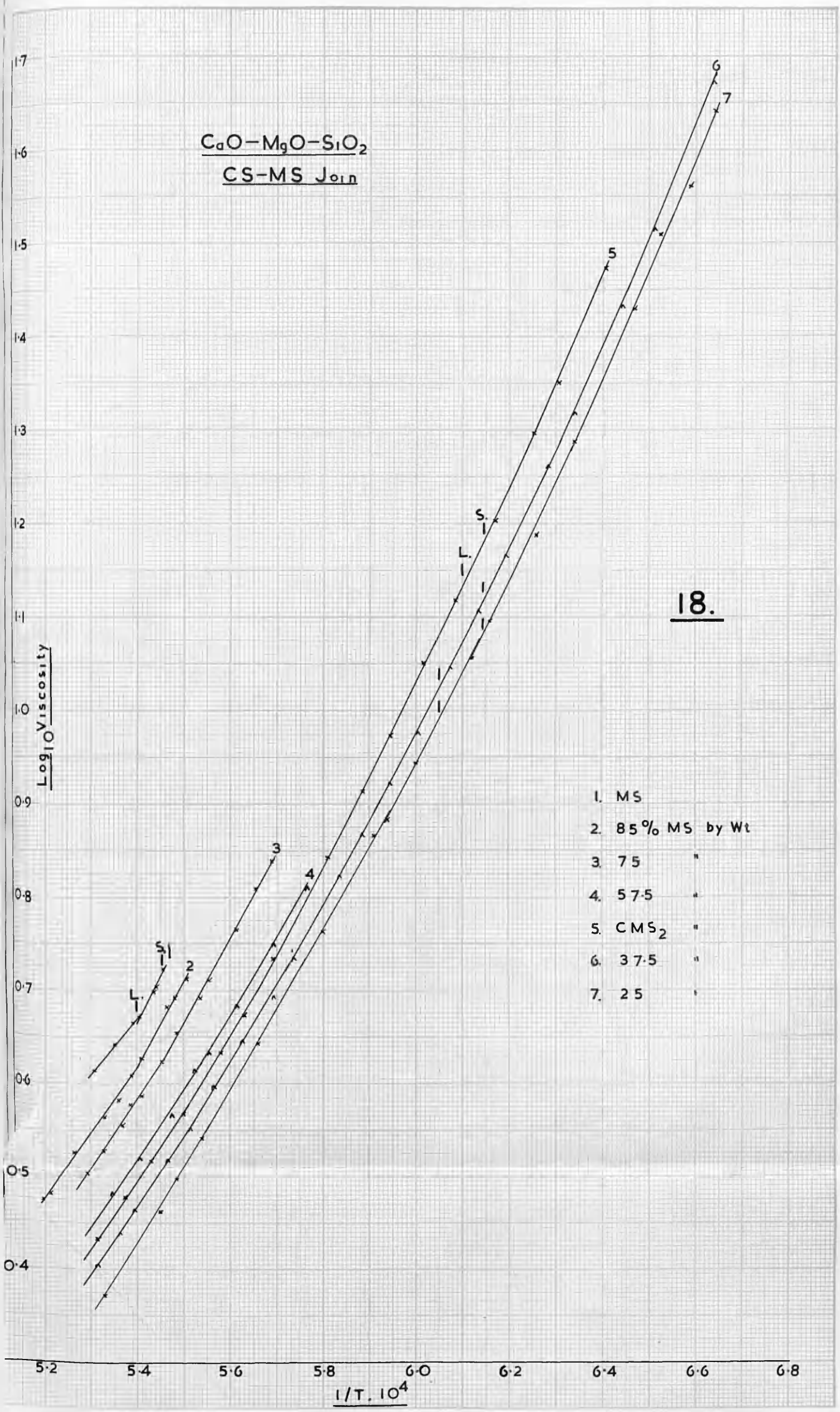
$CaO.SiO_2$-$MgO.SiO_2$.	% MS by Wt.	E_1
	25	37.5
	37.5	36.2
	CMS_2	35.2
	57.5	35.0
	75	34.1
	85	32.7
	MS	29.5

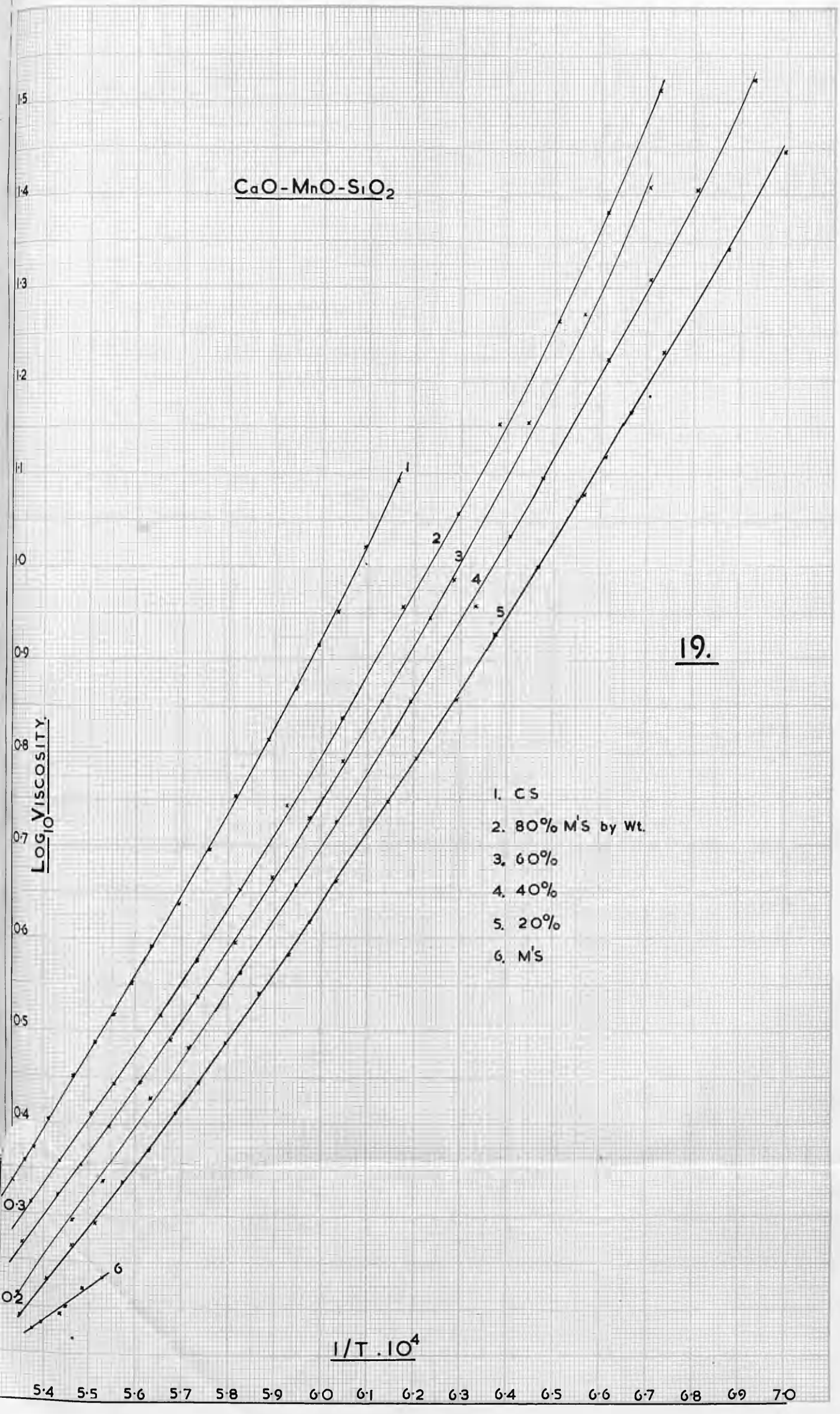
$CaO.SiO_2$-$MnO.SiO_2$.	% M'S by Wt.	E_1
	20	32.9
	40	30.6
	60	29.5
	80	28.3
	M'S	16.8



$CaO-SiO_2$

1. 65% SiO_2 by Wt.
2. 62·5. "
3. 60. "
4. 58. "
5. 56. "
6. 55·5. "
7. 54·5. "
8. 53·5. "
9. 52·5. "
10. 51·7. "
11. 50. "
12. 48. "


CaO–MgO–SiO2
CS–MS Join
18.
Log10 Viscosity
1/T. 10^4
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
L.
S.
1. MS
2. 85% MS by Wt
3. 75 "
4. 57.5 "
5. CMS2 "
6. 37.5 "
7. 25 "

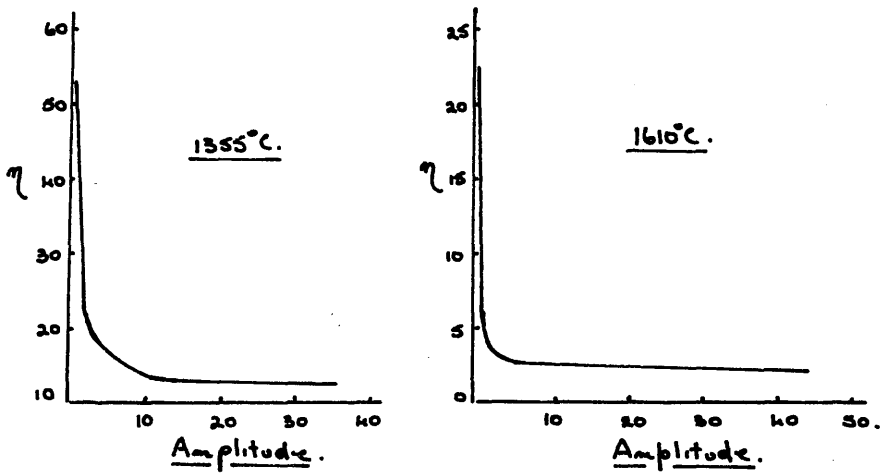

CaO-MnO-SiO2
19.
Log10 Viscosity.
1/T .10^4
1. CS
2. 80% M'S by Wt.
3. 60%
4. 40%
5. 20%
6. M'S
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
5.4
5.5
5.6
5.7
5.8
5.9
6.0
6.1
6.2
6.3
6.4
6.5
6.6
6.7
6.8
6.9
7.0

$CaO-MnO-SiO_2$ system the liquidus temperature across the metasilicate join is uncertain. The values of E_η so obtained are shown in Table 1.

As already indicated the log $\eta \sim 1/T$ relationship over the complete range of observed viscosity is shown in graphs 17,18, and 19 and indicates the strong deviation from linearity in the supercooled material. The form of these curves is considered later.

SECTION 2. VARIATION OF VISCOSITY WITH RATE OF SHEAR.

Interest in this point with respect to slags was initiated by the results published by Towers and Kay(45) on the $MnO-SiO_2$ system. They showed that for SiO_2 contents $\geq$ $MnO.SiO_2$ the viscosity was a variable with the rate of shear, higher viscosities being recorded at lower rates of shear. The type of variation in their results is shown below for $MnO.SiO_2$ at 1355°C and 1610°C.



The apparatus employed was of the logarithmic decrement system so that the rate of shear increased with increasing amplitude of oscillation. The results were explained as being due to the progressive breaking up of the silicate network as the rate of shear increased. That is, mechanical energy could achieve a similar effect on the silicate structure as an increase in temperature. This implies that fragments of silicate network are involved as units in the flow process.

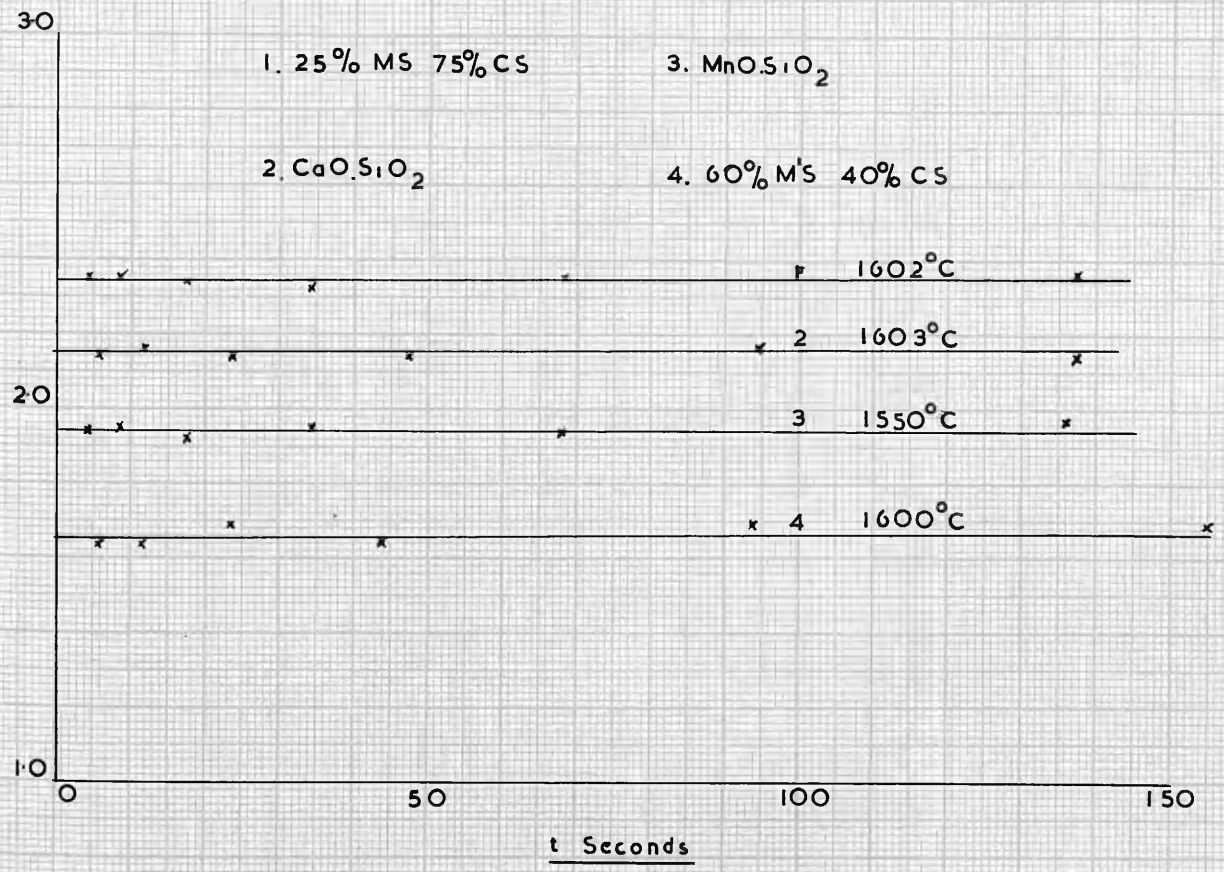
The size of these units is therefore taken to decrease as the rate of shear increased.

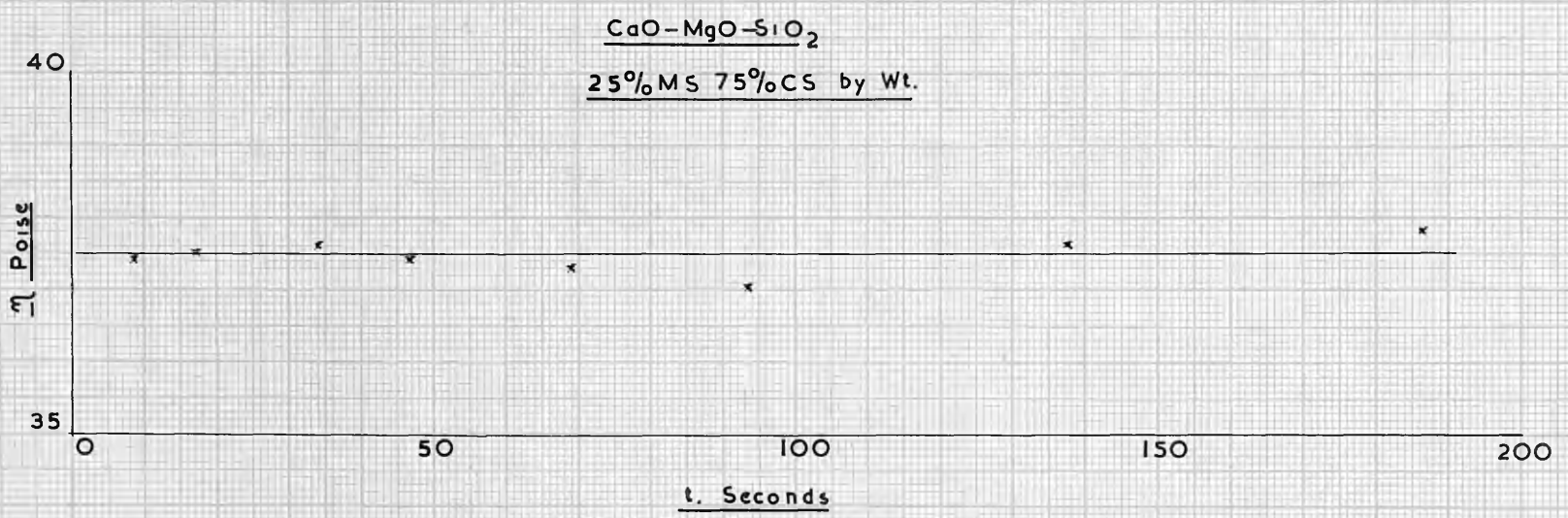
Work on the present apparatus with respect to rate of shear proved negative. No variation could be observed above the liquidus for any of the slags examined and the results on $MnO.SiO_2$ could not be confirmed. An example from each type of slag is shown - $CaO.SiO_2$; $MnO.SiO_2$; $CaO-MnO-SiO_2$ and $CaO-MgO-SiO_2$ - in graph 20.

Graph 21 shows the results for a supercooled lime-magnesia-silica slag (25% by weight $MgO.SiO_2$. 75% $CaO.SiO_2$). This slag cooled to a glass and in the supercooled condition gives no evidence of the viscosity changing with rate of shear. An effect was observed however on two slags, Rhodonite $MnO.SiO_2$ and the lime-silica 65% SiO_2, in the presence of separated silica. In both these instances, the viscosity showed an increase at lower rates of shear, although the results did tend to be erratic. In the $MnO.SiO_2$ at 1547°C a rise from 2.72 to 3.22 poise was observed and in the lime-silica at 1457°C a rise from 34.5 poise to 36.6 poise. This variation could be expected on the basis of a liquid system containing suspended solid and the effect has been observed before in slag systems; Volarovich[59] noted such a variation in his investigations on $Na_2O-B_2O_3$ liquids. This was put down to the presence of suspended solid. Both $MnO.SiO_2$ and the 65% SiO_2 ($CaO-SiO_2$) precipitate silica on cooling.

Viscosity – Rate of Shear

t=Period of Rev.^{n}



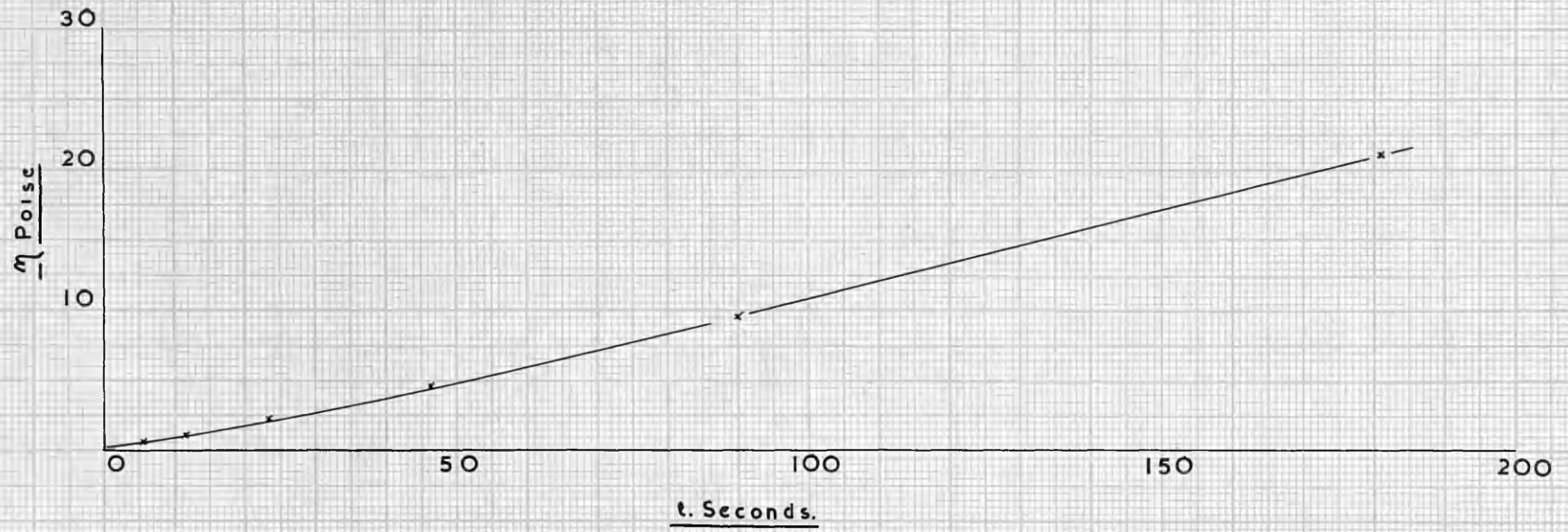

CaO – MgO – SiO2
25% MS 75% CS by Wt.
40
35
η Poise
0
50
100
150
200
t. Seconds

The results of Towers and Kay therefore become difficult to explain. The only possible reason would seem to be that the results were obtained in the presence of precipitated silica. The present work indicates that the liquidus temperature for $MnO.SiO_2$ is 1540°C and from the equilibrium diagram it can be seen that the liquidus curve must rise steeply to the immiscibility point. A slight error in composition could lead to the liquidus temperature being well above 1600°C in which case SiO_2 would be present. It was noticed in the present work that the SiO_2 which precipitated from the manganese slag collected as a grey skin on the surface. This was not so in the lime silica slag and is due of course to the difference in density between the SiO_2 and the manganese silicate liquid. The presence of this skin could lead to the results which were obtained.

As a check on the rotating cylinder viscometer a suspension of bentonite was made up, of a very dilute concentration. This is known to exhibit shear effect and was such that its viscosity was similar to those of the slags examined. The curve for this is shown in graph 22 and indicates the very rapid increase in viscosity as the rate of shear decreased.

From these experiments it is concluded that liquid slags show no variation in viscosity with rate of shear in the truly liquid condition. This result must

Bentonite Suspension



be regarded as consistent with the flow process in which the mechanism of flow involves units which are the ions themselves and not aggregates of ions. The viscous flow of these liquids can be accounted for satisfactorily on this basis. Variation with rate of shear would not therefore be expected.

A postulate of viscous flow involving the movement of simple ions rules out the possibility of variation with rate of shear in the manner suggested by Towers and Kay and this as indicated below is in agreement with the derivation of the Eyring equation for viscous flow.

$$\eta = \frac{h\lambda_1}{\lambda_2 \lambda_3 \lambda^2} e^{\Delta G/RT}$$

This equation only holds if $2kT \gg f\lambda_2\lambda_3\lambda$ where k = Boltzman's Constant = 1.4×10^{-16} ergs/degree and f = applied stress in dynes/cm^2. Values of stress existing at the surface of the inner cylinder in the rotating cylinder viscometer have been calculated here for viscosities of 1 poise and 1000 poise.

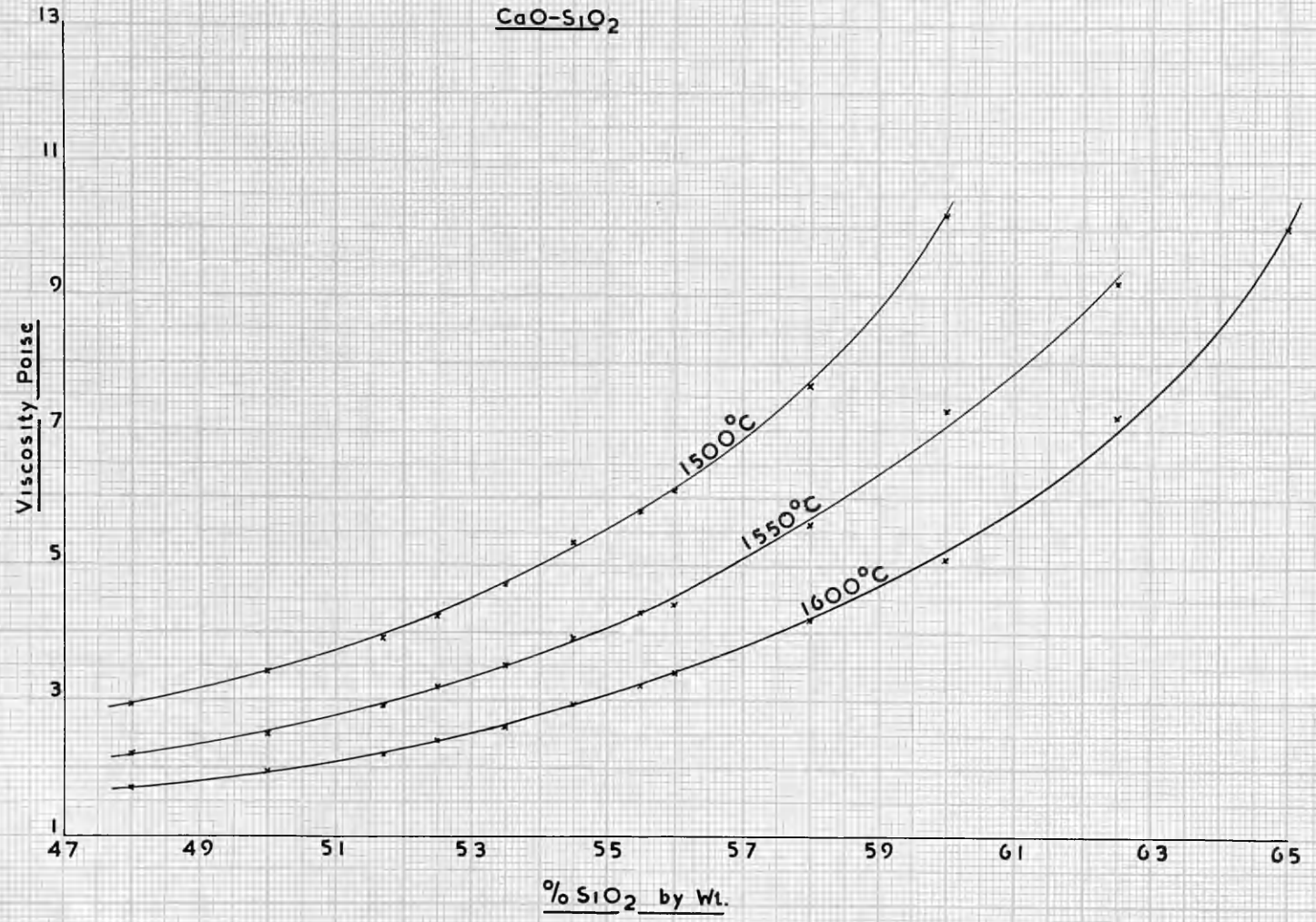
η	f	$f\lambda^3$ approx.	2kT approx.
1.0	1 dyne/cm^2	10^{-24} ergs.	10^{-13} ergs.
1000	1000 dyne/cm^2	10^{-21} ergs	10^{-13} ergs.

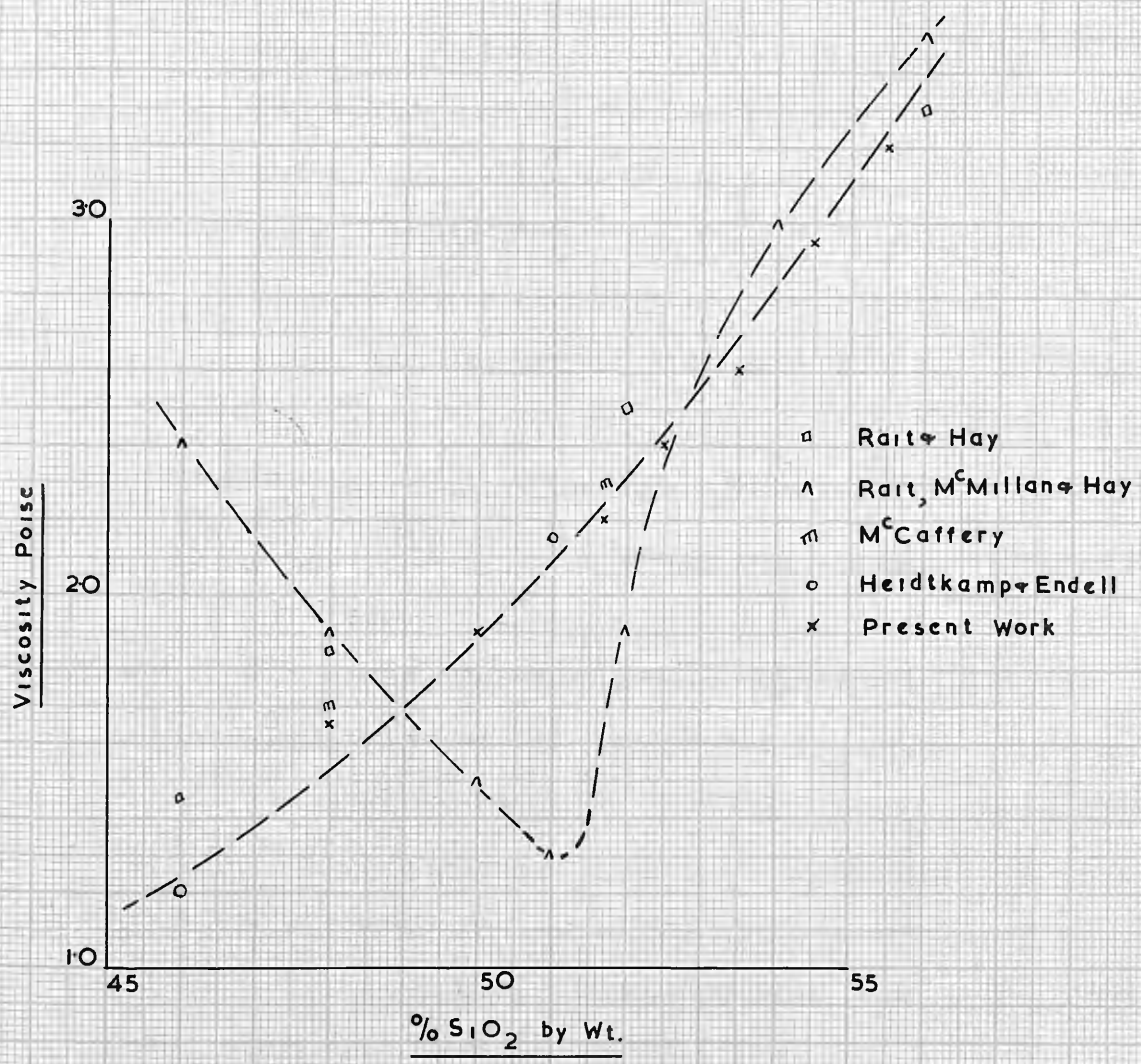
From these values, no variation in η would be expected with change in rate of shear although it is possible that similar experiments on glasses in which η rises to very high values (e.g. 10^{14} poise) would show a significant variation.

SECTION 3. VARIATION OF VISCOSITY WITH COMPOSITION.

Lime-Silica System. The variation of viscosity with composition is shown (graph 23) for the range 48 weight per cent silica to 65 weight per cent silica. The viscosity increases smoothly and continuously with increase in silica content and increases rapidly beyond the metasilicate composition. This rapid increase is a well known feature of silicate systems and is undoubtedly due to the increased structural bonding at higher silica contents.

Rait, McMillan and Hay(33) recorded the existence of a minimum value in the viscosity composition curve at the metasilicate composition $CaO.SiO_2$. This is not observed here. For the purposes of comparison, the values obtained by Heidtkamp and Endell(36), Rait and Hay(32), McCaffery and co-workers(35) and Rait, McMillan and Hay(33) are reproduced in graph 24, with those of the present work. C.H.Herty(34) also observed a minimum at $CaO.SiO_2$ but his results are 150% higher than any quoted above. It can be seen that fairly good agreement exists between the present work and that of the others with the exception of Rait, McMillan and Hay. Recently Machin and Hanna(39) have quoted a value of 2.33 poise for a slag of 45% SiO_2, 55% CaO at 1500°C. This is in good agreement with an extrapolated value of the present work. It must be concluded therefore that


CaO-SiO2
Viscosity Poise
13
11
9
7
5
3
1
1500°C
1550°C
1600°C
47
49
51
53
55
57
59
61
63
65
% SiO2 by Wt.


30
20
10
Viscosity Poise
45
50
55
% SiO_2 by Wt.
Rait & Hay
Rait, M^cMillan & Hay
M^cCaffery
Heidtkamp & Endell
Present Work

the viscosity - composition isotherms in the $CaO-SiO_2$ system show no minimum value at the metasilicate composition.

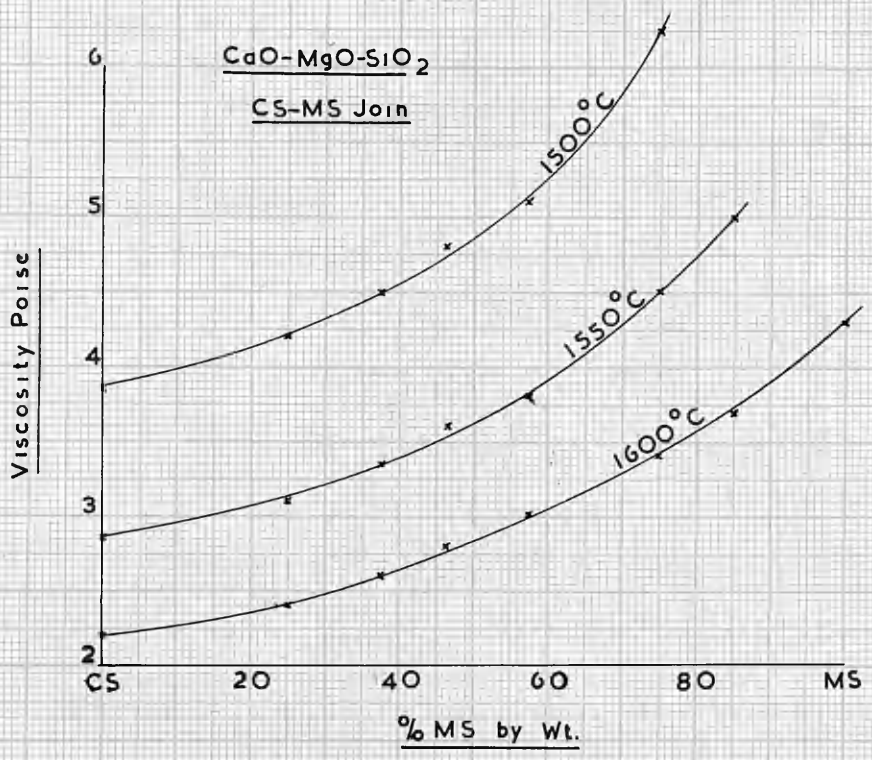
Preston(37) has postulated that in the Na_2O-SiO_2 system a maximum occurs between $Na_2O.SiO_2$ and $Na_2O.2SiO_2$ due to complex formation between these molecules. This implies that at those compound compositions these "molecules" move as units and between these compositions are hindered in their move-:ment by association with each other. However, this also leads to the implication that in pure silica viscous flow takes place by movement of molecules of silica and this is impossible in view of the structure of silica.

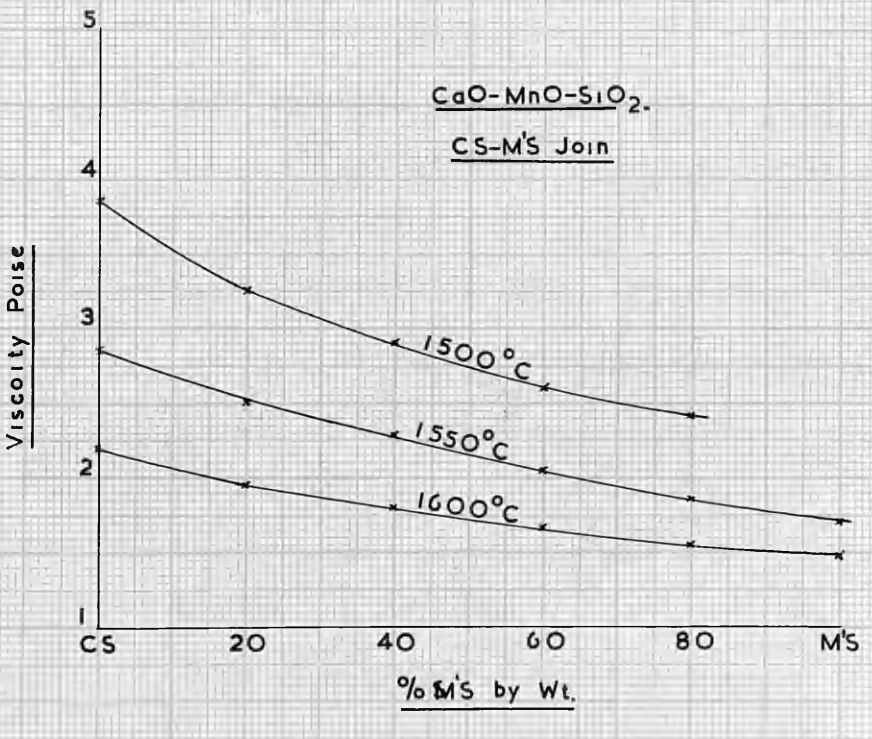
Considering that even in the solid state ionic materials are not considered in terms of molecules, it seems unnecessary to do so in the liquid state. It is the present view that the modern theories of liquid flow do not allow the occurrence of a maximum or a minimum in a binary system such as $CaO-SiO_2$ or Na_2O-SiO_2. One end member is characterised by high coordination and relatively weak bonding between ions and the other by low coordination and strongly directional bonding. Bernal has shown that the viscosity of a liquid is dependent on the configuration of the liquid and that the existence of low coordination as in ionic liquids, requires greater energy for a configurational change, i.e., higher viscosity. In a

system such as $CaO-SiO_2$, the continued addition of silica brings about continuously decreasing effective coordination in the liquid and an increase in the degree of directional bonding. On both these counts the viscosity should increase with increase in silica content and increase continuously across the system. The postulate of a process of flow involving the movement of silicate fragments or "molecules" is unnecessary. In the solid, the material is consid-:ered as an ordered array of positive and negative ions. In the liquid, a less ordered arrangement exists and flow can take place by the relative movement of the ions. High viscosity is due to the great inter-:action of ions on the freedom of others and this becomes extreme in pure silica. On this type of approach, the occurrence of a maximum or minimum is not expected and the present results must be considered in line with the modern views of viscous flow as applied to all classes of liquids.

<u>$CaO.SiO_2$-$MgO.SiO_2$.</u>

The change in viscosity which occurs when CaO is replaced by MgO at the metasilicate composition is seen in graph 25. There is a continuous rise from 2.2 poise at $CaO.SiO_2$ to 4.3 poise at $MgO.SiO_2$ for a temperature of 1600°C. As theory predicts there is no evidence of a maximum or minimum at the compound


CaO-MgO-SiO2
CS-MS Join
1500°C
1550°C
1600°C
Viscosity Poise
6
5
4
3
2
CS
20
40
60
80
MS
% MS by Wt.


CaO-MnO-SiO2.
CS-M'S Join
1500°C
1550°C
1600°C
Viscoity Poise
5
4
3
2
1
CS
20
40
60
80
M'S
% M'S by Wt.

composition $CaO.MgO.2SiO_2$. From the point of view of structure of the liquid, rather than consider the viscosity in poises, it is more pertinent to consider "equivalent viscosities" for the same number of cations/c.c. This has been done from values of density given by T.B.King(56).

ρ_{MS} = 2.39 gm/cc. Molar Volume = 100/2.39
= 42 c.c.

ρ_{CS} = 2.40 gm/c.c. Molar Volume = 116/2.40
= 48.3 c.c.

$MgO.SiO_2$. Number of Cations/c.c. = $\frac{2N}{42} = 0.286 \times 10^{23}$

η = 4.3 at 1600°C.

$CaO.SiO_2$ " " " " = $\frac{2N}{48.3} = 0.250 \times 10^{23}$

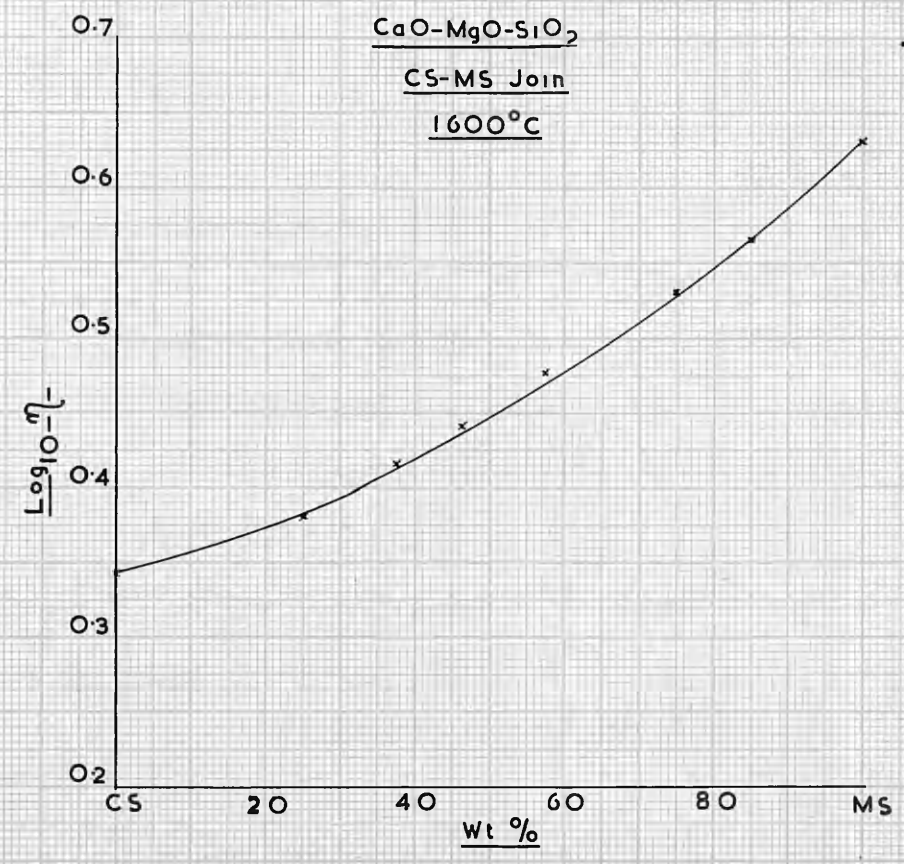
η = 2.2 at 1600°C.

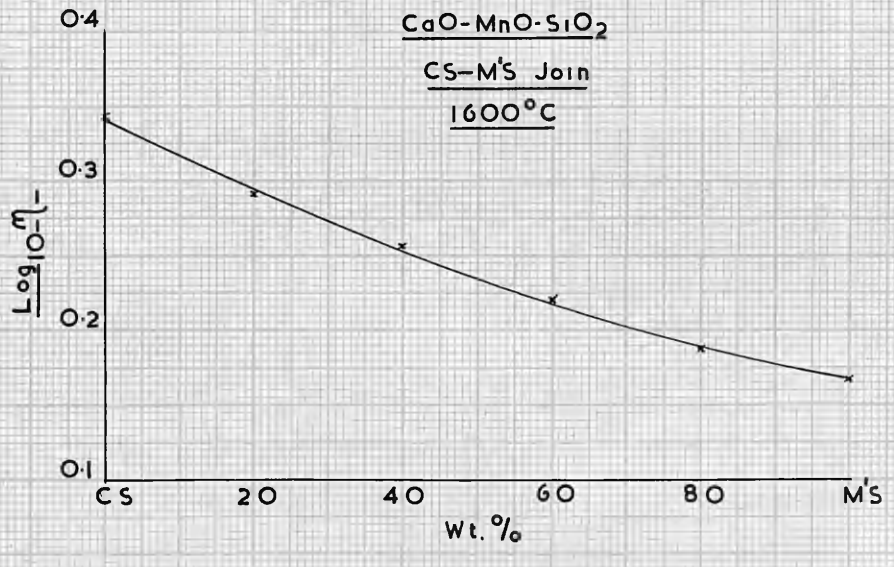
For the same number of cations per c.c., equivalent viscosities at 1600°C become

$MgO.SiO_2$	3.75
$CaO.SiO_2$	2.20

This value for $MgO.SiO_2$ is of course meaningless as far as the flow properties of the slag are concerned since different shearing areas are involved, but it does illustrate that the effect of the Mg^{2+} ion on the bonding within the liquid, as far as viscous flow is concerned, is less than at first apparent.

The relationship $\log_{10}\eta$ ~ composition for this metasilicate join is shown in graph 26. The plot is


CaO-MgO-SiO2
CS-MS Join
1600°C
0·7
0·6
0·5
0·4
0·3
0·2
Log10 η
CS
20
40
60
80
MS
Wt %


CaO-MnO-SiO2
CS–M'S Join
1600°C
0·4
0·3
0·2
0·1
Log10 η
CS
20
40
60
80
M'S
Wt. %

a smooth curve with no inflections and the form of the curve is not altered by plotting on a basis of equivalent viscosities for the same number of cations per c.c.

<u>$CaO.SiO_2$-$MnO.SiO_2$.</u>

In graph 25 the viscosity can be seen to decrease continuously from 2.2 poise at $CaO.SiO_2$ to 1.5 poise for $MnO.SiO_2$ - 1600°C. This may again be expressed as "equivalent viscosity" for the same number of cations per c.c.

$\rho\ MnO.SiO_2 = 3.1$ gm/c.c. Molar Volume $= \frac{131}{3.1} = 42.2$ c.c.

Number of Cations/c.c. $= 0.285 \times 10^{23}$

∴ "Equivalent Viscosities" are $CaO.SiO_2$ 2.2

$MnO.SiO_2$ 1.27

Manganese therefore very strongly reduces the effective bonding strength within the liquid. The relationship $\log_{10}\eta \sim$ composition is also shown for this metasilicate join and is similar in form to the lime-magnesium curve (graph 26).

The full significance of these results for metasilicates can be gained by reference to results on other silicate compositions. The work of Kozakevitch (41) indicates an extrapolated value of 1.5 poise for "$FeO.SiO_2$" at 1400°C. The values of ionic strength for these cations increase in the order $Ca^{2+} \rightarrow Mn^{2+} \rightarrow Fe^{2+} \rightarrow Mg^{2+}$ so that the general trend in this divalent class of ion would seem to be reduced viscosity at

higher ionic strengths. This has exception in the magnesium composition. A table of ionic strengths is shown below.

Monovalent Ions	C.N.	Radius A°	Ionic Strength
K^+	6	1.33	0.13
Na^+	6	0.98	0.19
Li^+	6	0.78	0.24
Divalent Ions			
Ba^{2+}	6	1.43	0.24
Ca^{2+}	6	1.06	0.33
Mn^{2+}	6	0.91	0.40
Fe^{2+}	6	0.83	0.43
Mg^{2+}	6	0.78	0.45
Trivalent Ions.			
Al^{3+}	6	0.57	0.84
Tetravalent Ions.			
Si^{4+}	4	0.39	1.57

The trend indicated above, that is, reduced viscosity at higher ionic strength also holds in the monovalent class. Thus Heidtkamp and Endell(36) point out that for $M_2O.2SiO_2$ melts at 1400°C the viscosity decreases in the order $K^+ \rightarrow Na^+ \rightarrow Li^+$ and this holds also at the metasilicate composition.

The anomalous result for the Mg^{2+} in the divalent class can only be explained by the entry of the Mg^{2+} ion into fourfold coordination. That is, rather than increasing the effective coordination within the

liquid, magnesium, compared with other divalent ions, is reducing it, and Bernal has shown that lower effective coordination requires greater energies for viscous flow. The following explanation is suggested for the observed decreased viscosity with increased ionic strength shown by each class of ion. This explanation is based on the theory that viscous flow in these liquids takes place by movement of simple ions and not aggregates of ions such as large complex silicate anions. The viscosity of these liquids must be dependent on the strength of the bond which the cations present make with oxygen. Since the Si-O bond is by far the strongest bond in these compositions it follows that for silica contents $\geqslant MO.SiO_2$, the viscosity will be in large part determined by the Si - O bonds. For a given state of coordination in the liquid the process of shear will involve so many Si - O bonds and so many M - O bonds. In the presence of an increasingly stronger M^{n+} ion the strength of the Si -O bond will be progressively weakened and the bonding strength distributed in a higher coordination system. The shear process then involves Si - O bonds which have been weakened and M - O bonds which have been strengthened. The strengthening however, is less than compensates for the weakening of the Si - O bonds due to the higher coordination of M^{n+}. This only holds true if constancy of coordina-

:tion is preserved as one M^{2+} ion replaces another. Deviations from the general trend therefore, as for Mg^{2+} indicate that this ion is taking up a coordina-:tion different from that of Ca^{2+}, Fe^{2+}, and Mn^{2+}. This can only be lower to account for the higher viscosity. The addition of a stronger ion does of course increase the overall bonding strength of the system but as far as viscous flow is concerned the effective bonding strength is reduced where differences in coordination exist in the liquid.

This anomalous behaviour of Mg^{2+} is not an iso-:lated instance. It has been reported to show anomalous behaviour in surface tension measurements (T.B.King)(12). In a study of the surface tension of silicate systems it was found that this property, for a given SiO_2 content, increased with increase in the ionic strength of the added cation. This is explained as being due to a dissociating effect of the stronger ions on the silicate network. In the case of Mg^{2+} and Fe^{2+} however the surface tension decreased. For Fe^{2+} the explanation was similar to that given for Mg^{2+} although it could also be due to the presence of some Fe^{3+} ions. Glass densities (M.L.Huggins)(57) and conductivity work (Bockris)(13) also indicate the anomalous behaviour of the Mg^{2+} ion. The behaviour of the Mg^{2+} is determined by its ionic environment. As

pointed out by Stanworth(6) a study of alumino-silicates of composition 2RO. Al_2O_3 $4SiO_2$ showed that the order of increasing viscosity is given by Mg → Zn → Ca → Sr → Ba. Here the Mg^{2+} is in line with the other cations and must be in a similar state of coordination.

One other point of interest here is the comparison of the present result for $CaO.SiO_2$ with $Na_2O.SiO_2$. The Na^+ and Ca^{2+} ions are of similar size (0.98A° and 1.06A° respectively) and the compounds have the viscosity value shown below.

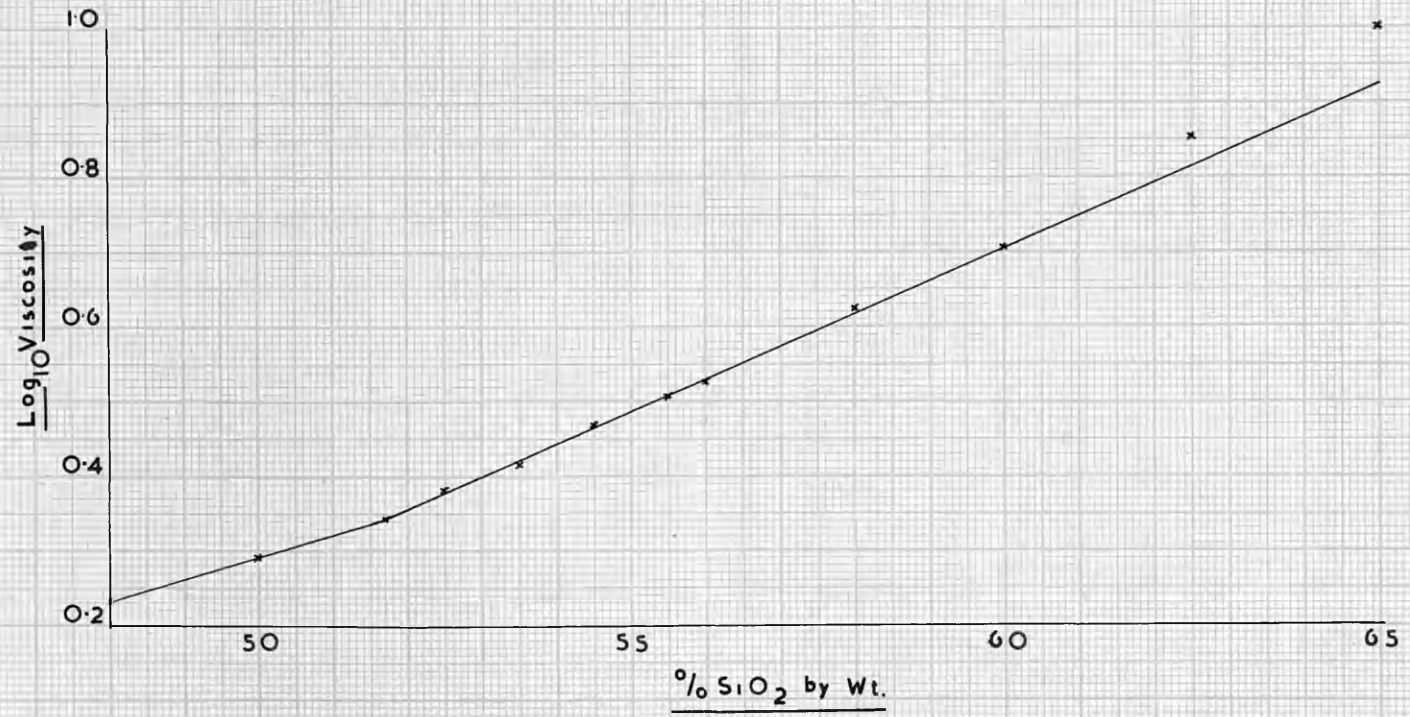
Compound	1600°C Poise.
$CaO.SiO_2$	2.2
$Na_2O.SiO_2$	1.0 (Extrapolated Value - Lillie).

Thus the increased ionic strength in Ca^{2+} has produced an increase in viscosity and not a decrease. From values of density both these compounds contain the same number of cations per c.c. in each case. In the sodium compound however this involves two Na^+ to one Si^{4+} while in the calcium compound the proportion of silicon ions involved in the shear process is higher $1Ca^{2+}/1Si^{4+}$. This shearing of a greater number of Si - O bonds in the calcium compound leads to the greater viscosity.

In the lime silica system the results have also been plotted on the basis of $\log \eta$ ~ composition.

CaO-SiO_2

Temp. 1600°C



This is shown in graph 27. There does seem to be a slight change in direction at the metasilicate although this is made more doubtful by the fact that the plot on the acid side deviates from a straight line at higher silica content. A change in direction would indicate a change in the conditions controlling flow and this might be expected on the basis that acid compositions are predominantly polymerised while basic compositions are not. As discussed later this predominance of polymerisation is associated with a more complex flow process and this could well become significant on passing the metasilicate composition.

SECTION 4. CHANGE IN THERMODYNAMIC FUNCTIONS FOR VISCOUS FLOW WITH CHANGE IN COMPOSITION.

Consideration of the results in this section will be made on the basis of the equation proposed by Eyring(20) for the process of viscous flow

$$\eta = A' e^{\Delta G/RT}$$

where A' = Constant

ΔG = Free Energy of Activation for Viscous Flow.

Eyring has evolved the equation $\eta = \frac{h \lambda_1}{\lambda_2 \lambda_3 \lambda^2} e^{\Delta G/RT}$

where h = Planck's Constant = 6.62×10^{-27} ergs.secs.

λ_1 = Distance between two units in the direction of flow.

λ_2 = " " " " at right angles to flow.

λ_3 = " " " moving layers.

λ = " " " positions of equilibrium in the direction of flow.

Knowing the values of λ, λ_1, λ_2 and λ_3 the free energy of activation for viscous flow can be calculated from the observed value of viscosity. In simple non polar liquids, the units of flow will probably be the molecules themselves and the distance between two positions of equilibrium merely the inter molecular distance. In such a case the different λ's may be considered approximately equal and the equation reduces to

$$\eta = \frac{hN}{V} e^{\Delta G/RT}$$

where V = Molar Volume (cc). N = Avogadro's No = 6.018×10^{23}.

In the silicate liquids considered here however, the situation is more difficult. The approach to the process of

flow, in the present work, is made on the basis that the ions themselves are the units of flow and not aggregates of ions. Even so the values of the different λ'_o can not be regarded as being equal. The value of λ_i would be a mean ionic diameter since ions of different radii are present. Also the distance λ between equilibrium positions is unknown. It is suggested here that this distance is the inter cationic distance, much greater than λ_i and dependent on the coordination of the system. The process of flow will necessitate the movement of cations from one equilibrium position to another similar equilibrium position and this is unlikely to be achieved inside the intercationic distance. Some information is available on interionic distances in glasses (B.E.Warren)(9) and approximate values of the above quantities could be obtained. However, the mechanism of flow is not yet known and to ascribe values to the various λ'_o on the basis of the above syggestions would be accompanied by some uncertainty. It is proposed therefore to employ here the same criterion as Eyring, namely, the molar volume since values of the density of these slags are available (T.B.King)(56).

It follows that no great significance can be attached to the actual values of ΔG and ΔS so obtained, but the trend in any one system can be regarded as significant. This method implies the assumption that the overall mechanism of flow for all the liquids examined here is the same. This is regarded as reasonable. The known values of

density are shown below and these have been used to compute approximate values of density for other slags.

Composition.	Density gm/cc.
$CaO.SiO_2$	2.40
44% CaO. 56% SiO_2	2.39
40% CaO. 60% SiO_2	2.38
25% $MgO.SiO_2$ / 75% $CaO.SiO_2$	2.40
$CaO.MgO.2SiO_2$	2.40
$MgO.SiO_2$	2.39
$MnO.SiO_2$	3.10

"Equivalent molecular weights" have been calculated and hence equivalent molar volumes. Thus the equivalent molar volume of the slag 44% CaO 56% SiO_2 is obtained

$$\text{Mols. of CaO/mol.}SiO_2 = \frac{44/56}{56/60} = .842$$

$$\therefore \text{Equivalent M. Wt.} = 1 \times 60 + 0.842 \times 56.$$

$$= 107.1$$

$$\text{Density} = 2.38 \text{ gm/cc.}$$

$$\therefore \text{Equivalent Molar Volume} = 45 \text{ c.c.}$$

The calculation for $CaO.SiO_2$ is shown for 1600°C

$$\eta = \frac{hN}{V} e^{\Delta G/RT}$$

$$\log_{10}\eta = \log_{10}\frac{hN}{V} + \frac{\Delta G}{4.6T}$$

$$\frac{hN}{V} = \frac{6.62 \times 10^{-27} \times 6.018 \times 10^{23}}{48.3} = 8.26 \times 10^{-5}$$

$$\log \frac{hN}{V} = -4.0830$$

$$\log_{10}\eta_{1600°C} = 0.3400$$

$$\therefore \frac{\Delta G}{4.6T} = 4.423 \qquad \Delta G = 38.2 \text{ k.cals./mol.}$$

Eyring has shown that the heat of activation ΔH can be obtained from the observed energy of activation E_η

$$\Delta H = E_\eta - RT$$

$$\Delta H = 36.8 - 3.7 = 33.1 \text{ k.cals/mol.}$$

$$\Delta G = \Delta H - T\Delta S$$

$$38200 = 33100 - 1873\,\Delta S.$$

$$\therefore \Delta S = -2.8 \text{ cals./degree.}$$

All other slags have been calculated on the same basis and the thermodynamic functions for all the slags are shown in Tables 2 and 3.

Energies of Activation for Viscous Flow.

The energy of activation for viscous flow is the total energy which is required in order that a unit act of flow can take place. Energies of activation have been obtained, as already shown, from the slope of the $\log \eta \sim 1/T$ relationship, and the values are used here for the purposes of calculation. Eyring has shown that in the molecular non polar class of liquid, E_η is largely composed of the energy required to provide the extra volume necessary for the formation of the activated complex in the flow process. In more complex liquids, this is not so, and the energy of activation will be composed of several increments involving the configurational changes during flow and the existence or non existence of directional bonding within the liquid. Typical energies of activation are shown below

Non Polar Liquid	E_η k.cals./mol.
C_2H_4	0.739
Hydroxyl Bonded Liquid	
H_2O	3.05
Ionic Liquid	
NaCl	9.1
KCl	7.4

The energies of activation for simple ionic liquids are considerably greater than for the other classes shown above. Here the flow process is more complex and will probably involve configurational changes associated with ionic clusters. Ward(22) has suggested that the energy of activation in this class of liquid will depend on the sum of the ionic radii; being large when the sum is small and vice versa. Thus $E_{NaCl} > E_{KCl}$ and this would suggest that E_η will vary, other factors being constant, with the repulsive forces between cations since the properties of any series of ionic liquids for a given anion is determined by the ionic strength of the cations present. This is in line with the views of Weyl(5) who has given a successful explanation of the melting points of many simple ionic compounds on this basis. The melting points of alkali chlorides are shown below

	M.Pt.
NaCl	800°C.
KCl.	770°C.
RbCl	710°C.

Just as the melting point is dependent on the energy required to move cations past one another and thus create the disorder of the liquid state, so the energy of activation for viscous flow in these simple ionic liquids could in part be determined by the same factor. In complex silicate liquids however this simple approach breaks down and the energy of activation is complicated by the irregular coordination which exists and the directional bonding associated with the powerful silicon ion. As will be shown, the influence of a stronger ion for a given molar content of silica is to reduce the energy of activation rather than increase it as in simple ionic liquids. This, however, must reach a limit as the strength of the added ion approaches that of the silicon ion.

The change in the energy of activation with composition is shown for each of the systems investigated. (Graphs 28 and 29). Compared to the values for simple liquids, E_η for these metasilicate liquids is considerably greater (e.g., $CaO.SiO_2$ 36.7 k.cal./mol.) and this is readily attributed to the low coordination and strong directional bonding of the silicon Si^{4+} ion. Greater energies are then required to break down the normal configuration as a prerequisite for viscous flow.

Lime-Silica.

The energy of activation is shown (graph 28) for a range in composition extending from 46 mol.% SiO_2 to 63 mol.% SiO_2. There appears to be a continuous relation-:ship between E_η and composition. There is no significant deflection at the metasilicate composition . The energy of activation increases with increase in SiO_2 content. This is in part due to the strong directional bonding of the Si^{4+} ion and this structural component is observed in the change in the value of ΔS, the entropy of activation for viscous flow. The existence of a "structure" within the liquid in the form of directional beonding which must be broken before flow occurs leads to the idea that the entropy of the activated state will be greater than that of the normal configuration. That is, the entropy of activation will become more positive for more structural liquids. Considering the nature of SiO_2 this is a reason-:able result for binary silicate systems and is found to hold true in the lime silicate system. This is similar to the explanation given by Eyring for the comparatively high energy of activation of water. The existence of hydrogen bonding in water has been proved and the positive entropy of activation obtained for water is explained by the break-:ing of those hydrogen bonds before flow can occur.

The increase in E_η observed for $CaO-SiO_2$ slags, however, is not completely due to the structural effect of

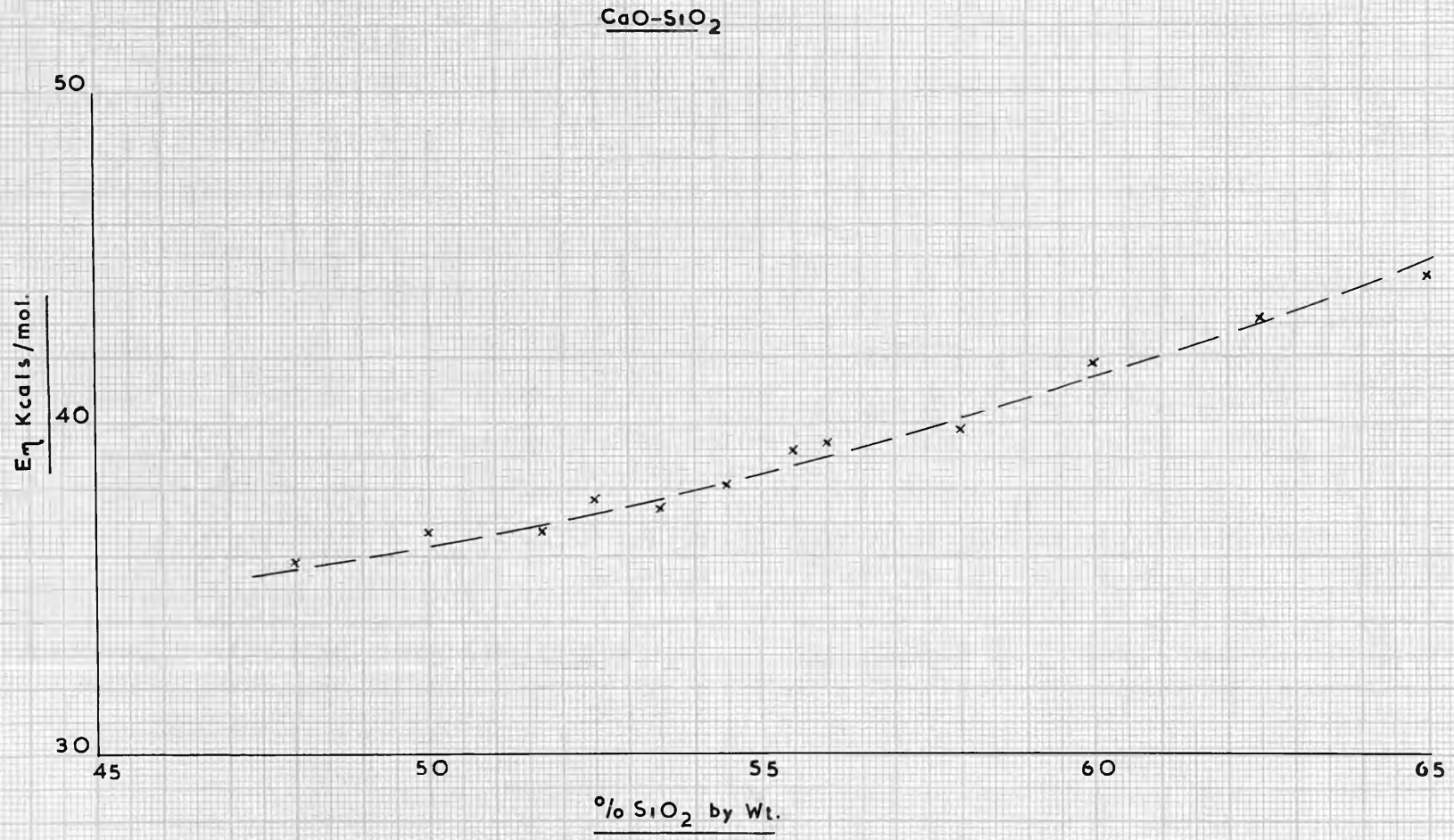

CaO-SiO2
50
40
30
Eη Kcals/mol.
45
50
55
60
65
% SiO2 by Wt.

TABLE 2.

Thermodynamic Functions for Viscous Flow.

Lime-Silica 1600°C.

Composition Weight % SiO_2.	E_η	K.cals./mol. ΔH	ΔG	ΔS cal/deg.
48	35.8	32.1	37.4	-2.8
50	36.7	33.0	37.6	-2.4
51.7(CS)	36.7	33.0	38.2	-2.8
52.5	37.7	34.0	38.4	-2.3
53.5	37.4	33.7	38.6	-2.6
54.5	38.1	34.4	38.5	-2.2
55.5	39.2	35.5	39.2	-1.9
56.0	39.4	35.7	39.5	-2.0
58.0	39.8	36.1	40.1	-2.1
60.0	41.8	38.1	40.7	-1.4
62.5	43.1	39.4	42.0	-1.4
65.0	44.4	40.7	43.0	-1.2

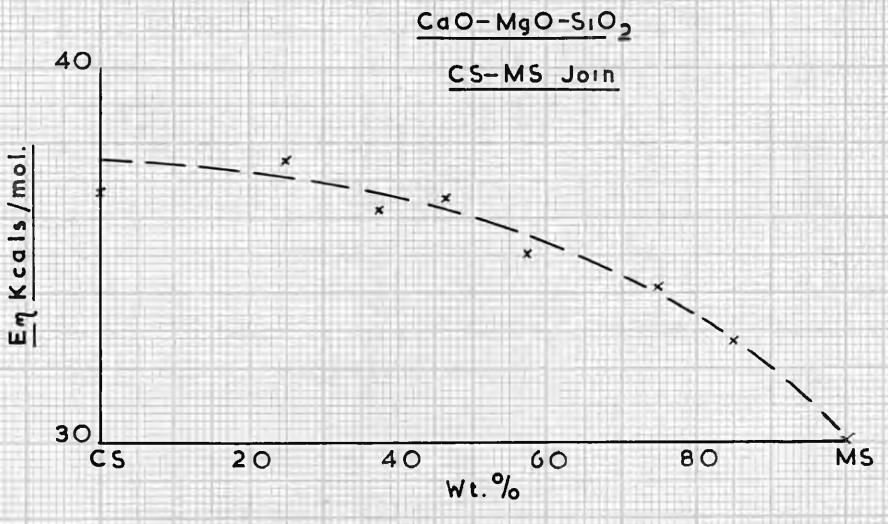
the silicate bonding as can be seen from the change in the free energies of activation. While the heat of activation varies over 8.7 k.cals/mol., the free energy of activation increases over 5.6 k.cals/mols. If the increase in E_η was due solely to structural effect the free energy of activation would remain roughly constant. This increase can be explained as in the case of simple ionic liquids by the greater repulsion between cations at the smaller interionic distances existing in the lower coordinated liquid of higher SiO_2 content.

<u>$CaO.SiO_2$-$MnO.SiO_2$</u>.

The energies of activation for viscous flow in mixtures of metasilicates decreases as the Ca^{2+} ion is replaced by the Mn^{2+} ion (graph 29). From a value of 36.8 k.cals/mol. at $CaO.SiO_2$ E_η drops to a low value of 16.8 k.cals. at $MnO.SiO_2$. Assuming the Mn^{2+} ion takes up the same coordination as the Ca^{2+} (i.e. 6) this reduction in E_η can only be due to the reduction of the structural effect of the silicon bonding. It is suggested therefore that the presence of an ion such as Mn^{2+} is powerful enough to decrease considerably the existence of silicate structure within the liquid. This is supported by the congruent melting point of $CaO.SiO_2$ and the incongruent melting point of $MnO.SiO_2$. Structural elements in liquid $CaO.SiO_2$ similar to that existing in the crystalline form would therefore be expected on the basis of this type of melting point.

A similar view was advanced by Dietzel[11] with regard to lime magnesia silicates. He considered that the ring structure shown by crystalline $CaO.SiO_2$ would be preserved in the liquid state. In considering the change from $CaO.SiO_2$ to $MgO.SiO_2$ which has an incongruent melting point he pointed out that while $CaO.SiO_2$ was built up by ring formation, $CaO.MgO.2SiO_2$ and $MgO.SiO_2$ had chain structures. This he ascribed to the presence of the more powerful Mg^{2+} ion and suggested that ring formation in metasilicates was only possible for cations of lower strength. For ionic strengths greater than Mg^{2+}, even the chain structure is unstable, e.g., $BeO.SiO_2$. Dietzel then considers that in melts of the $MgO.SiO_2$ system, single tetrahedra would exist for this composition. Actually such behaviour as suggested above is considered on the basis of the present results, to hold for the Mn^{2+} ion, but as is shown later the behaviour of the metasilicate liquid $MgO.SiO_2$ is more consistent with a polymerisation process. The results obtained here indicate that the highly directional character of the Si-O bonds is greatly reduced at this metasilicate composition by the Mn^{2+} ion. This is shown in the increasingly negative trend in the value of ΔS towards the Rhodonite composition.

The free energy of activation shows a slight decrease of 2 k.cals. across the join. In view of the fact that the Mn^{2+} ion is stronger than the Ca^{2+} ion this is opposite to what might be expected from the results on simple ionic


CaO-MgO-SiO2
CS-MS Join
40
30
Eη Kcals/mol.
CS
20
40
60
80
MS
Wt. %

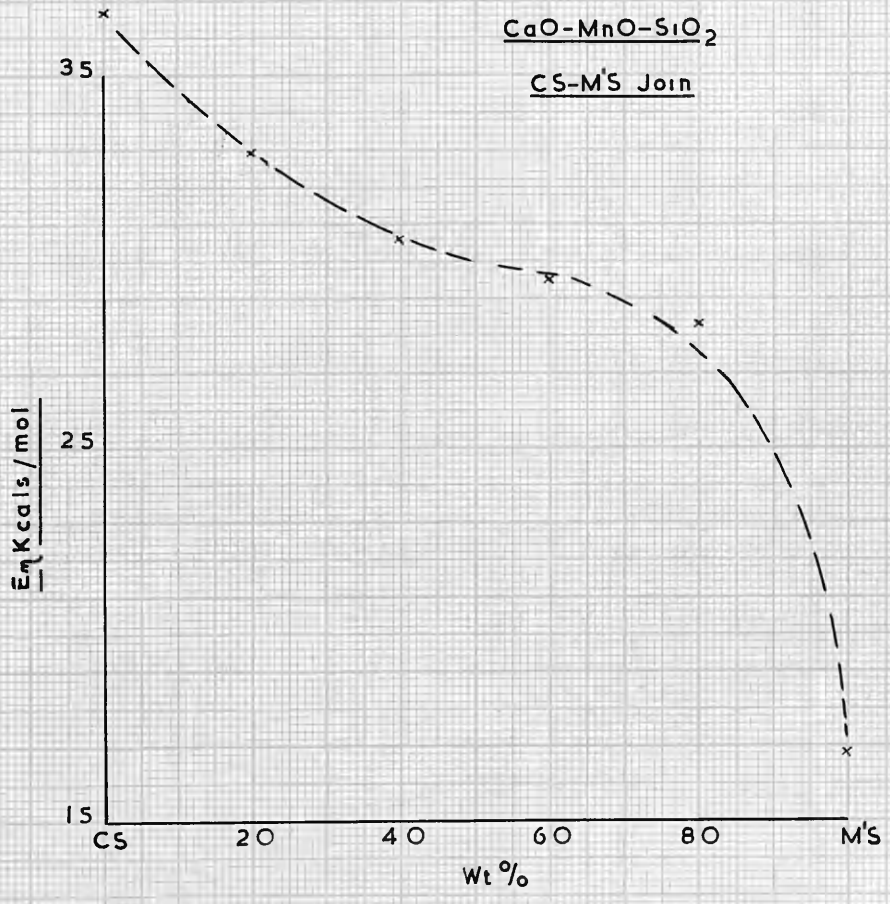

CaO-MnO-SiO2
CS-M'S Join
35
25
15
Eη Kcals/mol
CS
20
40
60
80
M'S
Wt %

TABLE 3.

Lime-Magnesia Silica. 1600°C.

Composition Weight % $MgO.SiO_2$.	E_2	K.cals./mol. ΔH	ΔG	ΔS cal./deg.
CS	36.7	33.0	38.2	-2.8
25	37.5	33.8	38.2	-2.3
37.5	36.2	32.5	38.4	-3.1
46.3 (CMS_2)	36.5	32.8	38.6	-3.1
57.5	35.0	31.3	38.8	-4.0
75.0	34.1	30.4	39.4	-4.8
85.0	32.7	29.0	39.6	-5.6
MS	30.0	25.8	40.0	-7.6
$CaO-MnO-SiO_2$.				
CS	36.7	33.1	38.2	-2.8
20	32.9	29.2	37.6	-4.5
40	30.6	26.9	37.2	-5.5
60	29.5	25.8	36.6	-5.8
80	28.3	24.6	36.4	-6.3
M'S	16.8	13.1	36.1	-12.2

liquids and on the lime silicates discussed. It is even possible that the strong Mn^{2+} ion, besides reducing the directional bonding associated with the Si^{4+} ion may also have the effect of slightly increasing the mean coordination of the Si^{4+} ion in the liquid. This would lead to a lower free energy of activation. However, in comparison to the heat of activation ΔG is almost constant so that the effect here is principally one of structure.

$CaO.SiO_2$-$MgO.SiO_2$.

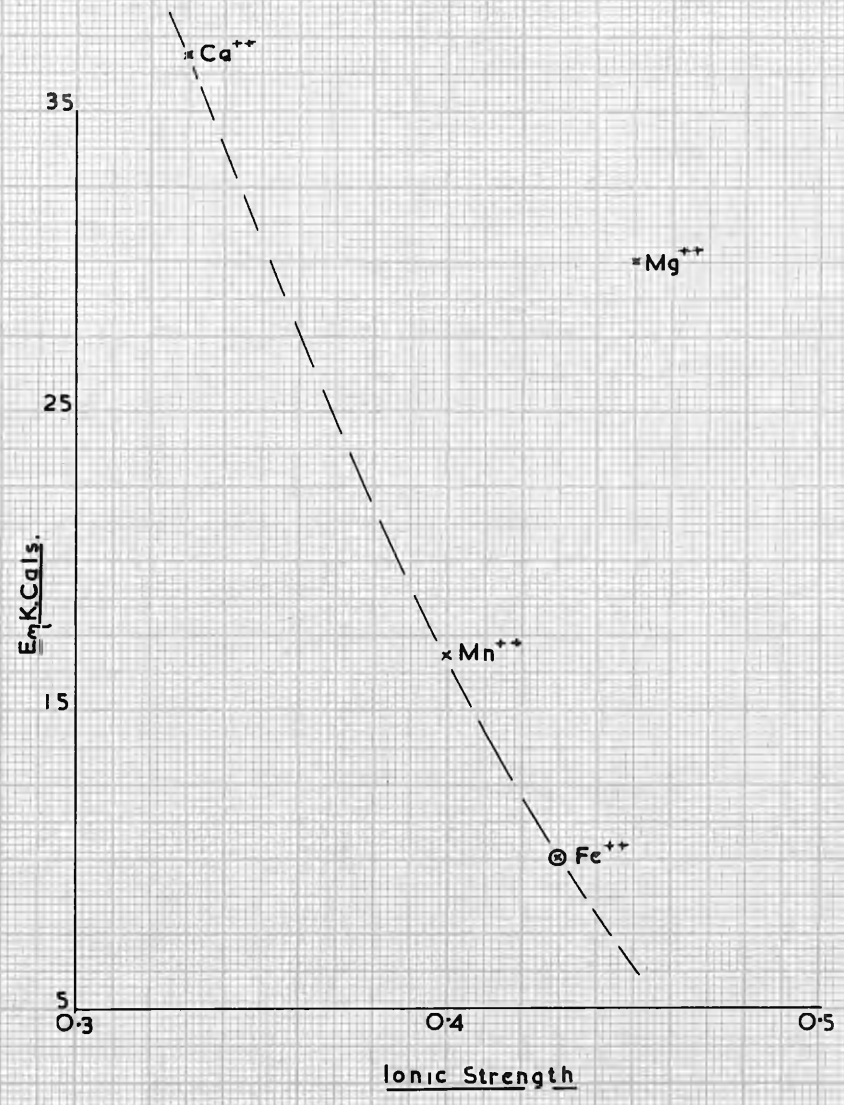
Results obtained from the examination of this join show that the energy of activation for viscous flow decreases from $CaO.SiO_2$ to $MgO.SiO_2$ and markedly so beyond the diopside composition $CaO.MgO.2SiO_2$ (graph 29).

Here again a change in composition from a compound of congruent melting point to one of incongruent melting point is being considered. The substitution of Ca^{2+} by Mg^{2+} has resulted in a lowering of the energy of activation and it is interesting to consider the variation of the energy of activation with ionic strength for these meta-:silicate compositions. For this purpose, the results of Kozakevitch(41) on iron silicates are included. Kozakevitch measured the viscosity of iron silicates up to 45 mol. per cent. silica at 1400°C. Calculation shows the slag of 45 mol. per cent silica to have an energy of activation of 8 k.cals./mol. The results on other slags

are not sufficiently good to allow an accurate extra-:polation to the composition "$FeO.SiO_2$" but the energy of activation must be close to 10 k.cals./mol. Taking this value, graph 30 relating E_η to ionic strength (based on 6 fold coordination) has been drawn.

On this basis, for the Mg^{2+} ion to be in sixfold coordination it would be expected to have an energy of activation for viscous flow lower than 10 k.cals. at the metasilicate composition. This may be compared with the observed value of 30.0 k.cals./mol. This large diff-:erence can only be ascribed to the entry of the Mg^{2+} ion into fourfold coordination and thus enhancing the existing silicate structure rather than destroying it. A higher coordination than four would be unlikely to cause such a large difference between the expected and the observed energies of activation. It is considered here that this is direct evidence for the entry of the Mg^{2+} ion into fourfold coordination.

This anomalous energy of activation for $MgO.SiO_2$ thus causes the viscosity for this composition to be greater than would be expected and therefore out of line with the general trend in any valent class of ion at constant SiO_2 content, i.e., progressive decrease in viscosity as the ionic strength of the cation which is present increases. In addition to this however, the viscosity of $MgO.SiO_2$ with E_η 30.0 k.cals. is greater than that for $CaO.SiO_2$ with E_η 36.8 k.cals. and this


Ca++
Mg++
Mn++
Fe++
35
25
15
5
E in K.Cals.
0·3
0·4
0·5
Ionic Strength

contrary to normal behaviour. In general, the variation in the viscosity of a series of liquids progressively changing in composition follows the variation in E_η. That is, increase in E_η results in increased viscosity and a decrease in E_η, decreased viscosity. In the equation

$$\eta = A' e^{-\Delta S/R} e^{E_\eta/RT}$$

a reduction in E_η due to elimination of structural bonding e.g., as in water with rise in temperature, means a smaller value of ΔS and therefore an increase in the term $e^{-\Delta S/R}$ However, the viscosity still falls since the contribution of this term is small compared to the E_η term. Therefore in $MgO.SiO_2$ with E_η 30.0 kcals. we should expect η to lie below the value for $CaO.SiO_2$. That it does not means that the term $e^{-\Delta S/R}$ is much larger than is consistent with the value of E_η. An explanation for this can be obtained in the light of the treatment given by R.M.Barrer (19) in his "zone theory" of activation for viscous flow.

From a consideration of the equation

$$\eta = A e^{E_\eta/RT}$$

Barrer has shown that there is a functional relationship between E_η and -log A at constant temperature. The term A is a function of the size of the zone of activation taking part in the flow process and involves the term $e^{-\Delta S/R}$ which takes account of the changes in entropy of the system in attaining the activated state. Barrer has shown that the entropy change ΔS is composed of two

parts, one positive and varying with E_η and the other negative

$$\Delta S = BE_\eta - \varphi \qquad B = \text{Constant.}$$

The positive component is concerned with the increased entropy due to structural breakdown during flow. The negative component takes account of the amount of synchronisation or cooperative effort required between moving units which enables the flow process to occur. It can therefore be regarded as a probability factor and is dependent on the nature of the liquid. In a normal series of liquids one of those terms is generally constant usually the probability term. Barrer has shown, however, that in polymerised melts more complex relations are taking place in the process of flow and that these polymer-:ised melts are characterised by a more negative value of ΔS, i.e., a larger value of A compared to simple liquids for a given E_η.

In the change of composition from $CaO.SiO_2$ both effects are operative. That is due to the entry of the Mg^{2+} ion into 4 fold coordination the positive component of ΔS is much greater than would have been expected and the negative term is also greater as a result of the polymerisation brought about by the same factor. The negative term appears to become of greater significance beyond the diopside composition and the viscosity continues to increase while the energy of activation decreases. The question arises as to what extent

the Mg^{2+} ion is in four fold coordination at this composit-:ion $MgO.SiO_2$. The fact that E_η for $MgO.SiO_2$ is less than for $CaO.SiO_2$ indicates that not all the Mg^{2+} ions are in four fold coordination. These present in higher coordination must be acting strongly to reduce E_η. However, since E_η is still high, the proportion of the high coordinated Mg^{2+} ions must be small. From the equilibrium diagram $MgO-SiO_2$ it can be seen that $MgO.SiO_2$ at the peritectic reaction temperature dissociates to give a small proportion of Forsterite $2MgO.SiO_2$ and a high proportion of liquid richer in SiO_2. The structure of orthosilicates is known to consist of individual $(SiO_4)^{4-}$ tetrahedra with the other cations present in six fold coordination. It is suggested here therefore that the Mg^{2+} ions associated with the Forsterite formed at the peritectic reaction temperature remain in six fold coordination, the remainder and the majority going into the four fold arrangement. In such a case, the predominance of the polymerised material explains the results obtained here.

The viscous flow of $MgO.SiO_2$ therefore when considered as one of a series therefore is analogous to the "slow" chemical reactions as discussed by Eyring(20) in his theory of absolute reaction rates. In many chemical reactions although the heat of activation is small the reaction is much slower than expected due to the complex phase relations which take place during reaction. The

case of $MgO.SiO_2$ has a parallel in the viscous flow of polyesters(20). In these, as the molecular weight increases, the viscosity increases continously while the energy of activation remains constant at 8 k.cals./mol. This is explained in a similar manner to the explanation given for $MgO.SiO_2$, i.e., a more complex flow process in the higher polyesters.

It can also be seen from the thermodynamic functions for lime magnesia silicates that the free energy of activation increases slightly with change of composition from $CaO.SiO_2$ to $MgO.SiO_2$. It is suggested again that this is due to the closer approach of cations in the lower coordinated structure.

Relationship between the Energy of Activation for Viscous Flow and the Heat of Fusion.

J.D. Bernal(18) has shown that melting involves a change of configuration within the material. The latent heat of fusion is small when the configurations of solid and liquid are similar and large when the two configurations are widely different. The heat of fusion is therefore a measure of the energy required to bring about the configurational change from the ordered to the disordered state. Viscous flow may also be regarded as a breakdown of an existing configuration during the activated process and so some relationship might be expected between the energies for these two processes for liquids of the same structural type. This has been examined by Ward(22) for several classes of liquids and is done here for some metasilicate compositions.

Compound.	ΔH_f	E_η	$E_\eta/\Delta H_f$
$MnO.SiO_2$	8.7	16.8	1.96
$CaO.MgO.2SiO_2$	18.5	36.5	1.97
$CaO.SiO_2$	(13.4) - 19.8	36.8	2.75 or 1.86
$MgO.SiO_2$	14.4	30.0	2.10

The values of the heats of fusion have been taken from Kelley(59) and from Kubaschewski and Evans(60). Kelley quotes a value of 13.4 k.cals. for $CaO.SiO_2$. However, Kubaschewski gives an alternative value of 19.8 k.cals. considered more accurate and this would seem likely from

the values of the ratio $E_\eta/\Delta H_f$ for the other compounds. None of the values of ΔH_f is considered of great reliability but even so, considering the accuracy of determining both E_η and ΔH_f the constancy of the relationship is remarkable. The ratios for these liquids may be compared with those for simple ionic liquids.

Compound	ΔH_f	E_η	$E_\eta/\Delta H_f$
NaCl	7.2	9.1	1.26
KCl	6.4	7.4	1.15

These lower ratios would indicate that the configurational changes in melting and in viscous flow are of a similar nature for these liquids. This would seem reasonable for those comparatively simple structures. In the silicate liquid this is apparently not holding true. Here the configurational changes in flow are involving greater energies. This rough correspondence between E_η and ΔH_f for liquids of the same structural type holds throughout all classes of liquids and demonstrates the similar nature of the melting mechanism and the flow mechanism. It also provides support for the assumption made earlier that the mechanism of flow in liquids of the same structural type is similar.

Work of Cohesion and Energy of Activation for Viscous Flow.

The concept of the work of choesion is due to Harkins(61) and defined by him

Work of Cohesion = 2 x Surface Energy

If γ = Surface Energy in cals./unit area.

N = Avogardro's No. V = Molar Volume

$(V/N)^{\frac{2}{3}}$ = Surface of Area occupied by 1 mol.

$\therefore$ No. of mols./unit surface area = $(N/V)^{\frac{2}{3}}$

Surface Energy/mol. = $\gamma (V/N)^{\frac{2}{3}}$

$\therefore$ Molar Surface Energy = $\gamma(V/N)^{\frac{2}{3}} N = \gamma V^{\frac{2}{3}} N^{\frac{1}{3}}$

$\therefore$ Molar Work of Cohesion = $2\gamma V^{\frac{2}{3}} N^{\frac{1}{3}}$

If γ is expressed in dynes/cm. then

$\therefore$ W , Molar Work of Cohesion = $2.\ 2.39.\ 10^{-8}\ V^{\frac{2}{3}}\ N^{\frac{1}{3}}$ cals.

Grunberg and Nissan(62) have made the observation that the ratio E/W is approximately unity for a large number of normal liquids, e.g., benzene 1.086. For these liquids the ratio remains unaltered with temperature.

For associated liquids, this no longer holds true and the ratio reaches higher values and changes with temperature

	E/W.
Water	2.29 at 0°C 1.70 at 100°C.
CH_3OH	2.23 at 0°C.

This can be explained by the fact that the work of cohesion as calculated from surface tension does not involve increments of energy due to dissociation of

associated complexes within the liquid. The process of viscous flow does, and the ratio then alters with temper-:ature e.g., H_2O, due to a change in the degree of association.

The value of this ratio therefore may be taken as direct evidence for the existence of associated complexes within the liquid, complexes moreover which are broken down during viscous flow. This relationship has been calculated for the slags examined here from the surface tension measurements of King(12). The results are shown in Tables 4 and 5 for a temperature of 1600°C.

<u>CaO.SiO$_2$.</u> Molar Volume = 48.3 c.c. $N = 6.018 \times 10^{23}$

$$\gamma = 401 \text{ dynes/cm.}$$

$$W = 2.\ 2.39.\ 10^{-8}\ \gamma\ V^{\frac{2}{3}}\ N^{\frac{1}{3}}$$

$$= 2.\ 2.39.\ 10^{-8}\ 401\ (48.3)^{\frac{2}{3}}\ (6.016 \times 10^{23})^{\frac{1}{3}}$$

$$= 21.3 \text{ k.cals.}$$

$E_\eta = 36.8$ k.cals. $\therefore$ $E_\eta/W = 1.72$.

<u>Lime-Silica.</u>

The trend in the value of E_η/W clearly demonstrates the increasing degree of association within the liquid as the silica content increases. This method of gaining an insight into the structure of the liquid particularly emphasises the presence of associated complexes. The The presence of these causes a reduction in W and an incr-:ease in E_η. The fact that E/W is considerably greater than unity can also be taken as good evidence that

TABLE 4.

Relationship between the Work of Cohesion and the Energy of Activation.

Lime-Silica. 1600°C.

Composition. Weight %.	E_η k.cals.	W. k.cals.	E_η/W
48	35.8	23	1.56
50	36.7	21.4	1.72
51.7	36.7	21.4	1.72
52.5	37.7	21.0	1.79
53.5	37.4	20.8	1.81
54.5	38.1	20.7	1.84
55.5	39.2	20.5	1.91
56.0	39.4	20.3	1.94
58.0	39.8	18.9	2.10
60.0	41.8	17.6	2.37
62.5	43.1	17.2	2.51
65.0	44.4	14.9	2.98

viscous flow in these liquids is by the relative movement of simple ions as units of flow and not by the movement of large silicate anions. This latter was the view taken up by E. Seddon(63) who considered that viscous flow involved the movement of aggregates of ions as the units of flow. As the degree of association increased by increasing the silica content or by lowering the temper-:ature the size of aggregate which moved as a unit increased. This would require greater energies of activation. On this basis, however, since the flow process would not involve the breaking of bonds within the associated aggregate, it would be expected that the ratio E/W would remain at a value close to unity. That flow takes place by the movement of simple ions is also the approach made by Douglas(64) in his theory of viscosity for glasses.

<u>$CaO.SiO_2$ - $MnO.SiO_2$.</u>

Here the value of E/W decreases continuously from 1.72 for $CaO.SiO_2$ to 0.83 for $MnO.SiO_2$. It would seem therefore that the presence of Mn^{2+} is sufficient to destroy any network effect within the liquid at this composition. It is noteworthy that W remains roughly constant across the join where it might have been expected to show an increase. This however is not so.

TABLE 5.

Lime-Magnesia-Silica 1600°C.

Composition Weight % MS.	E_η k.cals.	W k.cals.	E_η/W .
CS	36.7	21.3	1.72
25	37.5	20.2	1.86
37.5	36.2	19.9	1.82
46.3(CMS_2)	36.5	19.75	1.85
57.5	35.0	19.6	1.79
75.0	34.1	19.4	1.76
85.0	32.7	19.2	1.70
MS	30.0	19.1	1.58

Lime-Manganous Oxide-Silica. 1600°C.

Weight % $MnO.SiO_2$	E_η k.cals.	W k.cals.	E_η/W
CS	36.7	21.3	1.72
20	32.9	21.2	1.56
40	30.6	21.4	1.43
60	29.5	21.5	1.37
80	28.3	21.6	1.31
MS	16.8	20.3	0.83

$MgO.SiO_2$ - $CaO.SiO_2$.

The values for this range of composition demonstrates again the entry of the Mg^{2+} ion into fourfold coordination. The ratio E/W remains significantly above unity right across the metasilicate join. The values of W show a small but significant decrease to $MgO.SiO_2$ consistent with increasing polymerisation while E_η varies in the manner described previously.

The values of E/W obtained here may be compared with those for other liquids and for $FeO.SiO_2$. Taking E_η for $FeO.SiO_2$ = 10 k.cals. and γ = 363 dynes/cm.(12), E/W has a value of 0.53. The values of some simple ionic liquids are shown below.

Compound.	E/W.
NaCl	1.78
KCl	1.42
$NaNO_3$	0.61
KNO_3	0.69
AgCl	0.43
AgBr	0.48

B.S. Harrap and E. Heymann(23) have expressed considerable doubt regarding the values obtained for NaCl and KCl on the basis of the uncertainty in the values of E_η. Considering the comparatively simple structure of these compounds this would seem likely. However, it can be seen that E/W can fall considerably below unity

in which case the energy for viscous flow is less than the energy required for surface formation. The signi-:ficance of this is not immediately apparent but a possible reason may be in the fact that the relationship between E_η and W is not a strict one since E_η is a total energy while W is a free energy. A relationship between $\Delta G_{visc.}$ and W would show a truer significance. However, as indicated earlier, the derivation of for the ionic liquids considered here involved assumpt-:ions valid only for purposes of comparison.

It is convenient to summarise here the signifi-:cance of the foregoing considerations from the structural point of view for these metasilicate melts. Results from surface tension, conductivity and viscosity all show the same trend, that is, an increase in ionic strength of the added cation increasingly removes the effect of network structure within the liquid. As shown in the present work and in the other fields of work the exception to this is Mg^{2+} and as already pointed out this behaviour of Mg^{2+} will not necessarily hold over all compositions in the $MgO-SiO_2$ system. Thus as pointed out by T.B.King(12), Mg^{2+} is unlikely to behave in this fashion at the orthosilicate composition and Dietzel(65) has shown that in glasses of high SiO_2 content, Mg^{2+} behaves uniformly in a general trend with the other divalent cations in determining surface properties. Some conductivity functions and surface

tension data are shown with the viscosity data for the purposes of comparison. Surface tension data are taken from T.B.King(12) and conductivity data from Bockris et alia(13).

Composition	$\eta_{1600°C}$	E_η	$\gamma_{1600°C}$	$\Lambda_{1750°C}$	ΔH_Λ
CaO.SiO2	2.2	36.8	400	18.4	20.0
$MnO.SiO_2$	1.5	16.6	415	35.1	16.0
$FeO.SiO_2$	1.0 (1400°C)	(10.0)	363	44.0	15.0
$MgO.SiO_2$	4.3	30.4	378	12.2	24.0

In the surface tension work, the Fe^{2+} ion would also appear to be anomalous. This may be due to the presence of some Fe^{3+} ions. Results on metasilicates therefore indicate quite clearly that the divalent cation has a dominant contribution to make to the properties of the liquid. The presence of a strong ion such as Mn^{2+} or Fe^{2+} would seem to remove completely the effect of any silicate structure. This is in line with the view put forward by M.Rey(66) who considers that the presence of an ion such as Fe^{2+} is sufficient to prevent an oxygen ion O^{2-} from taking part in the silicate structure as such. It is also noteworthy that "FeO.SiO2" does not exist, even in the solid state. In the presence of Mn^{2+} or Fe^{2+} therefore, the metasilicate approaches more closely to the behaviour of simple ionic liquids.

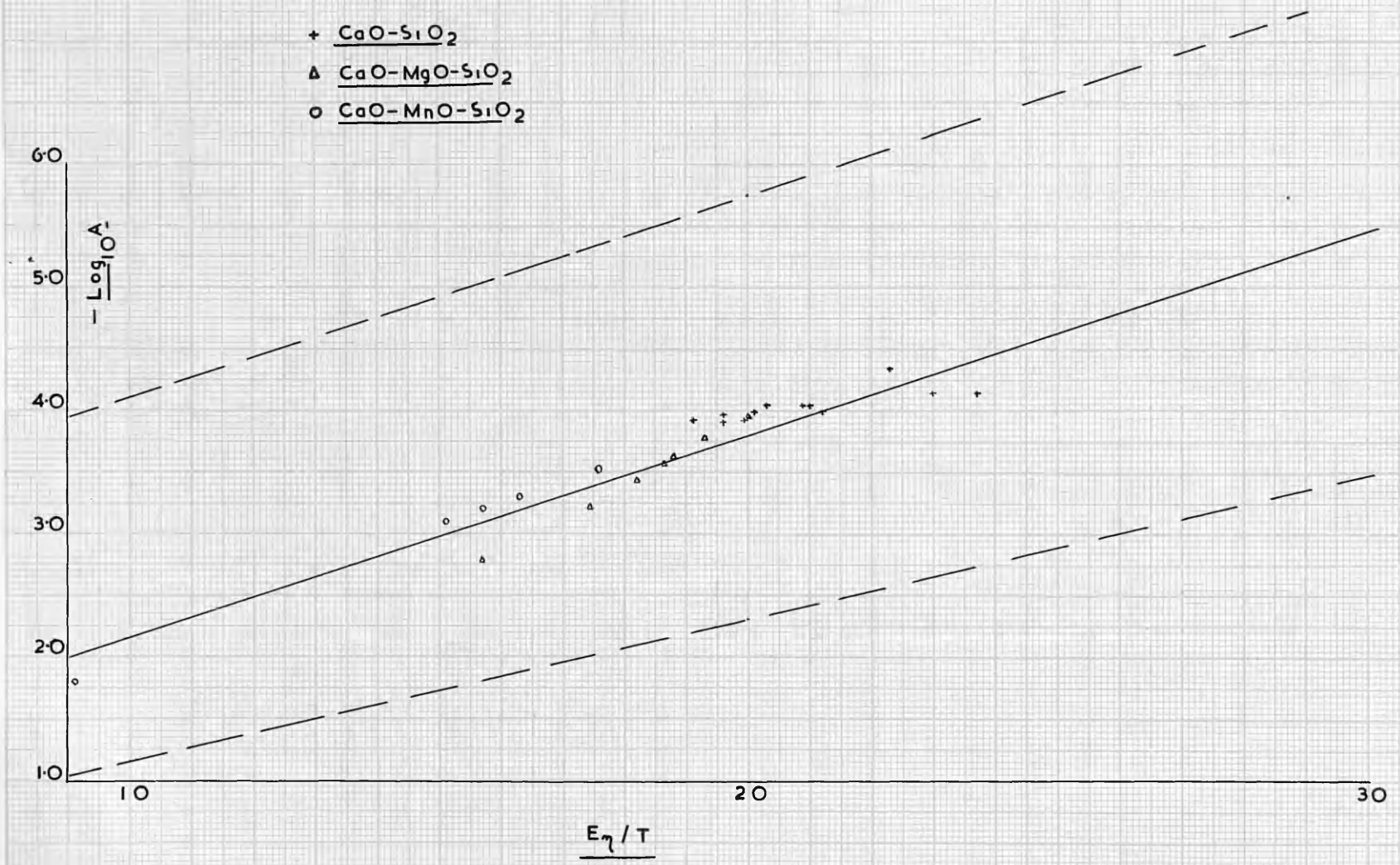
SECTION 5. DISCUSSION ON THE MECHANISM OF FLOW.

The theory of Eyring(20) has sufficiently established the fact that the process of viscous flow can be approached successfully on the basis of reaction rates. The flow process may be considered as a change at a definite rate from a normal configuration through an activated configuration to a second normal configuration. The energy required and the probability of attaining the activated complex determines the rate of reaction, i.e., the viscosity of the liquid. In the Arrhenius equation $\eta = A e^{E_\eta/RT}$ the A term contains two factors which can vary for different liquids.

(1) A factor dependent on the size of the moving unit.

(2) An entropy term dependent on structure within the liquid and the cooperative effort required between moving units for a successful unit act of flow.

The second term is the least clearly understood and until a complete mathematical solution of the liquid state is available, interpretations of it can only be approximate. As pointed out previously R.M.Barrer(19) in his "zone theory of viscous flow" has shown that there is a functional relationship between (- log A) and E_η at constant temperature. This relationship is reproduced in graph 31. The upper line (- log A = 2.43 + 0.167 E_η/T) is the median line for a large variety of liquids - simple molecular liquids, polar liquids, hydrogen bonded liquids,


+ CaO-SiO2
Δ CaO-MgO-SiO2
o CaO-MnO-SiO2
6·0
5·0
4·0
3·0
2·0
1·0
− Log10A'
10
20
30
Eη / T

metallic liquids and simple ionic liquids. Highly polymerised melts conformed to the lower line (- log A = 0.115 E_η/T) and these consisted of silicates, alumino-:silicates, borates and phosphates all very high in the structural component, i.e., SiO_2, P_2O_5, B_2O_3, etc. A considerable degree of scatter exists about these lines. Flow takes place by absorption of energy of activation E_η within each zone to cause a reorientation and readjustment amounting to a unit act of flow. The term (- log A) is a function of the size of the zone of activation. High values of E_η indicate large zones of activation, i.e., a large zone of activation is given by a small value of A brought about by a more positive value of ΔS. However, that the line for polymerised melts is below that for simple liquids is not due to smaller zones of activation but to a more complex flow process, i.e., a more negative ΔS for a given value of E_η.

The liquids in the present work have been included in the graph and can be seen to lie midway between the two general lines. The line through these has the equation - log A = 0.52 + 0.164 E_η/T. That these liquids lie midway between the other two lines is a reasonable result in that they may be considered semi-polymerised being of metasilicate composition. This type of plot gives a general picture for all classes of liquids and that such a functional relationship exists indicates that the cooperative effort or negative component of ΔS is

roughly constant for the majority of liquid classes. Variations can arise however, as indicated in the present results for $MgO.SiO_2$., where the liquids can show considerable variation between polymerisation and non polymerisation depending on composition.

On this theory therefore, flow in these liquids is by movement of simple ions and the present results can be explained on this basis as considered in the foregoing sections. That flow is by simple ions is supported by work on diffusion. Thus Towers, Paris and Chipman(67) obtained values of the diffusion coefficient D from viscosity results in rough agreement with their measured values in a $CaO-Al_2O_3-SiO_2$ slag. This could be done by the Stokes-Einstein relationship.

$$D = \frac{kT}{\eta\lambda}$$

where k = Boltzman's Constant λ = Distance between two equilibrium positions.

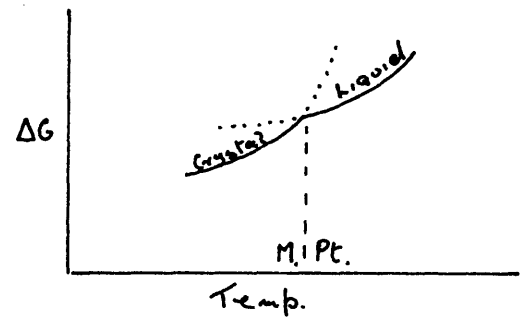
For their calculation, they used a value of $\lambda = 3A^{\circ}$. No agreement would have been obtained if the unit of flow were a large complex anion in which case λ would be much larger. It is noteworthy that $3A^{\circ}$ is the approximate cation-cation distance in these melts and this was suggested earlier in this work as the probable distance between equilibrium positions in the flow process.

SECTION 6. SUPERCOOLING AND THE RELATIONSHIP log $\eta \sim 1/T$.

SECTION 6. SUPERCOOLING AND THE RELATIONSHIP log $\eta \sim 1/T$.

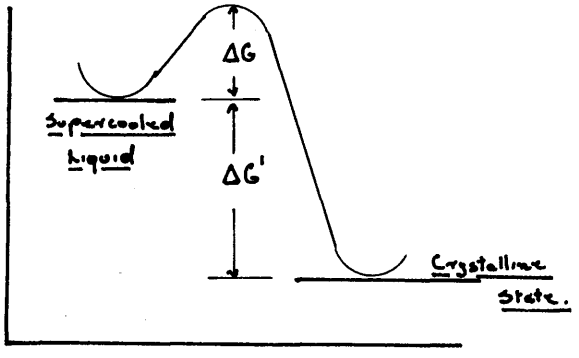
Almost all the slags examined showed a considerable degree of supercooling and log $\eta \sim 1/T$ curves have been shown (graphs 17,18 and 19). Liquidus and solidus temper-:atures have been marked in where possible. It can be seen that measurements have been made at temperatures well below that at which solidification should have occurred. Also the change in the relationship log $\eta \sim 1/T$ is smooth and continuous over the whole temperature range. The tendency of the slags to supercool showed certain qualitative singularities. Thus supercooling is a minimum at the compound compositions $CaO.SiO_2$, $MgO.SiO_2$, $MnO.SiO_2$. Of these three only $CaO.SiO_2$ showed any supercooling although it always crystallised at approximately between 1300°C and 1350°C (Melting point 1540°C).

The property of supercooling can be considered qualitatively in the following way. The free energy temperature relationship of any system shows a break at the melting point



If the system remains liquid below the melting point a certain degree of disorder persists and the system has a higher free

energy than in its stable crystalline state. This is indicated by the dotted curve in the diagram. The difference in free energy between the unstable supercooled liquid and the stable crystalline material acts as a driving force for crystallisation. Thus the tendency to crystallise always exists and becomes greater as the temperature falls. However, for this to occur the atoms have to move into the ordered positions of the crystal and this requires energy of activation. This can be represented by a diagram



ΔG = Free energy of Activation.

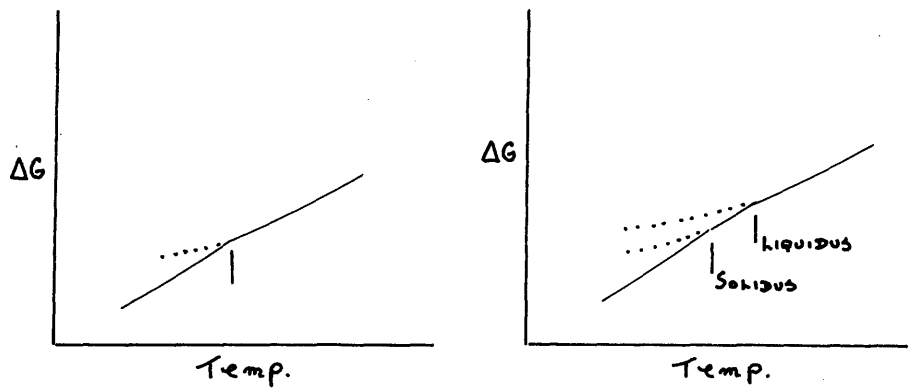
$\Delta G'$ = Difference in free energy between supercooled and crystalline states.

As a general qualitative statement, it can be said that if $\Delta G' > \Delta G$ then the system will crystallise. If $\Delta G' < \Delta G$ it will supercool and if the two are roughly equal then the system will be very sensitive to the conditions prevailing during cooling, e.g., rate of cooling, vibration. All other conditions being constant, the change in ΔG and $\Delta G'$ with temperature will determine the temperature at which crystallisation occurs.

The energy term ΔG is the free energy of activation of diffusion for the components of the liquid. In silicate liquids crystallisation will involve the rearrangement of silicate anions and the movement of smaller cations and the

overall process will require considerable activation energy even in the truly liquid condition. Thus the energy of activation E for diffusion of lime in Lime-Alumina-Silica slags is of the order of 20/30 k.cals. per mol. (McCallum and Barrott)(68) and Towers, Paris and Chipman(67) have observed a free energy of activation for diffusion of Ca^{2+} of 36.6 k.cals. in a slag of 40% CaO. 40% SiO_2 and 20% Al_2O_3. It is not surprising therefore that supercooling occurs readily even at metasilicate composition.

That $CaO.SiO_2$ should supercool while $MgO.SiO_2$ and $MnO.SiO_2$ do not, can be qualitatively explained on the above basis. The compound CaO.SiO2 has a congruent melting point; $MgO.SiO_2$ and $MnO.SiO_2$ have incongruent melting points. The free energy temperature diagrams for a congruent compound and an incongruent compound are shown below.



For materials of the same structural type the slope of the free energy temperature curve in the crystalline and truly liquid condition will be similar. In the incongruent compound however the free energy of the system continually increases during melting and the unstable supercooled state

has an extra increment of free energy due to this fact. The incongruent compound will therefore have a greater tendency to crystallise. This is a reasonable result since an incongruent melting point in itself indicates the great instability of the ordered crystalline state at high temper-:atures and of the disordered liquid state at low temper-:atures.

The degree of supercooling was greatest at compositions between compounds. Thus the slags 25% $MgO.SiO_2$ 75% $CaO.SiO_2$; 60% $MnO.SiO_2$ 40% $CaO.SiO_2$ and 40% $MnO.SiO_2$ 60% $CaO.SiO_2$ cooled completely to glasses. This is in line with the views of Dietzel(11) who suggested that the glass forming tendency would increase as the percentage of primary material which should crystallise decreased, i.e., for materials which can form glasses. Glassiness would therefore be a maximum at a eutectic composition and this is certainly indicated in the 25% $MgO.SiO_2$ 75% $CaO.SiO_2$ slag. This composition is very near the eutectic between $CaO.SiO_2$ and $CaO.MgO.2SiO_2$.

The degree of supercooling decreased rapidly beyond $CaO.MgO.2SiO_2$ to a minimum at $MgO.SiO_2$. This is consistent with the increasingly unstable state of the liquid condition when supercooled, as the Mg^{2+} ion increasingly enters four cold coordination to the compound $MgO.SiO_2$.

The slags of the $CaO.SiO_2$-$MnO.SiO_2$ join showed the greatest degree of supercooling up to the 60% $CaO.SiO_2$ slag. The published diagram of Voos(55) shows an unbroken solid solution series.from $CaO.SiO_2$ to $MnO.SiO_2$. This, however, is uncertain. Another diagram of Sundius(55) incorporates the compound bustamite $CaO.MnO.2SiO_2$ and a eutectic between $CaO.MnO.2SiO_2$ and $MnO.SiO_2$. This compound is known to exist in the mineral condition (White)(55).

The log $\eta \sim 1/T$ relationship.

A non linear log $\eta \sim 1/T$ plot is shown by all the slags which supercooled. The temperature at which any one particular slag "crystallised" from the supercooled state was not constant for repeated runs. It varied with the amount of time taken over the run and the treatment of the slag during the run. It is significant, however, that the viscosity curve was always the same. Thus if a slag supercooled to a greater degree on a repeat determination then the new values obtained yielded a smooth continuation of the original curve. The value of viscosity for the degree of supercooling observed here was also independent of the time taken to make a measurement. Thus a reading repeated after an interval of 2 hours yielded the same result. The time required to establish the equilibrium structure on those supercooled liquids is therefore negligible compared to that required to take a measurement. The smooth continuous form of the log $\eta \sim 1/T$ relationship indicates that no radical change is taking place on cooling. The atomic arrangement in the supercooled state is therefore similar to that in the liquid state.

The plot log $\eta \sim 1/T$ is linear above the liquidus for the $CaO-SiO_2$ and $CaO-MnO-SiO_2$ slags. A further variation in slope at much higher temperatures however cannot be discounted. Non-linearity of the log $\eta \sim 1/T$ plot is undoubtedly due to structural rearrangements within the

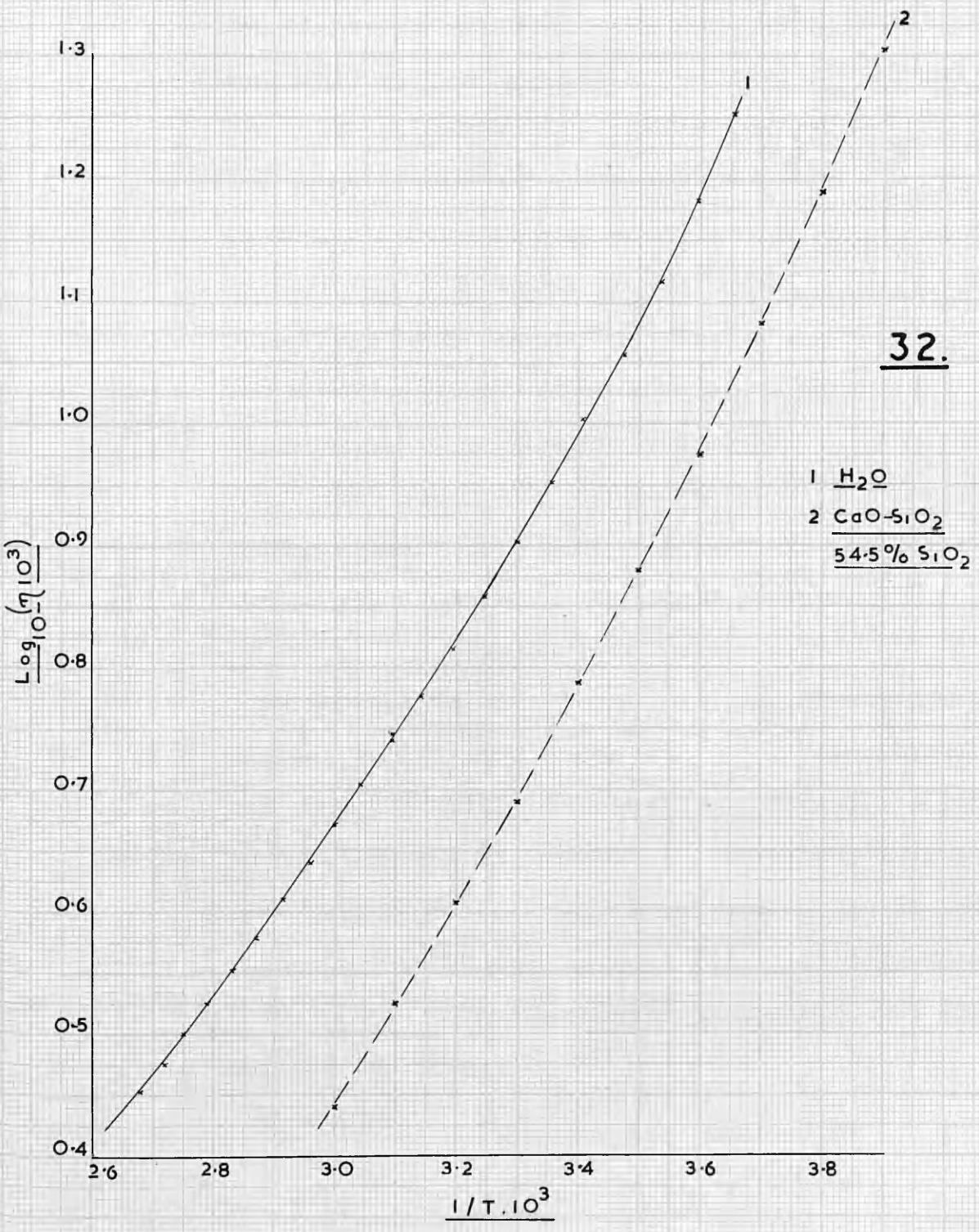
system as the temperature is changed. That it becomes linear in the truly liquid state means that these structural rearrangements have reached a limit or at least have become of no significance in affecting the temperature variation of the viscous properties of the liquid.

In the lime magnesia silica slags a slight variation in slope is observed above the liquidus temperature. It has already been deomonstrated that the Mg^{2+} ion at this metasilicate composition exists in a state of low coordination and this enhances the existence of structure in the liquid. At higher temperatures this tendency will decrease and the Mg^{2+} ion will strive to achieve higher coordination. The variation in slope therefore can be explained by the breaking up of the low coordinated structure as the temperature is increased. That such an effect does occur in silicate liquids is indicated by surface tension work (T.B.King)(12).

All the supercooled slags showed non-linearity below the liquidus temperature and the form of the curves is very similar to that for water. The curve for water is reproduced in graph 32. Andrade(69) has expressed the change of the viscosity of water with temperature by the expression

$$\eta = 4{\cdot}33.10^{-5} e^{3{\cdot}11/RT} \left(1 + e^{12{\cdot}1 - 0{\cdot}477T}\right)$$

The curves for the slags examined here can be put in the form of a similar equation. The equation for the 50% CaO.50% SiO_2 slag is shown below



1 H_2O

2 $CaO-SiO_2$

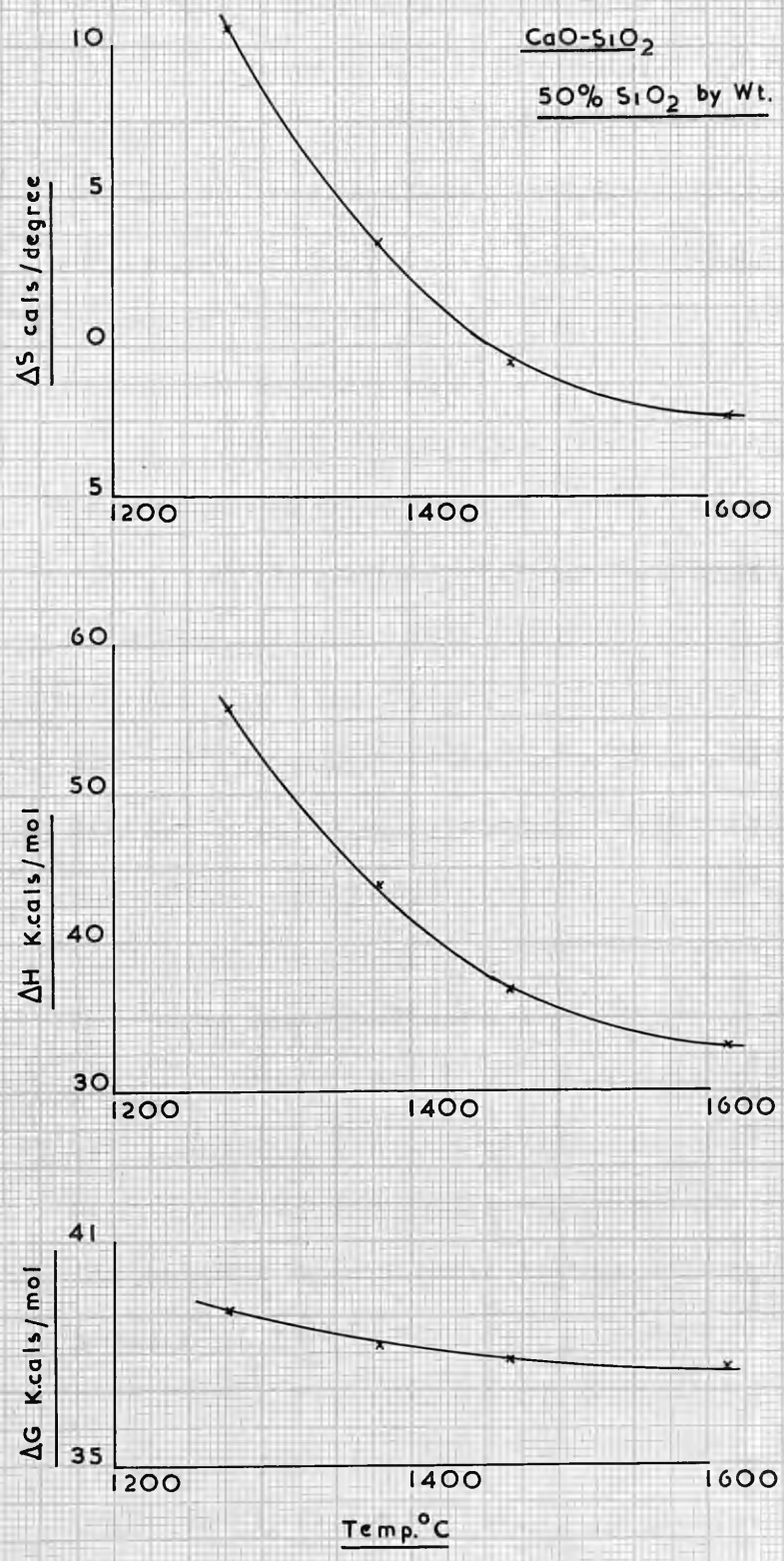
54·5% SiO_2

$$\eta = 1.035.\ 10^{-4}\, e^{36.8/RT}\left(1 + e^{21.99 - 0.0146\,T.}\right)$$

Equations for the other slags gave similar values of constants with no significant variation with composition. Non linearity of the log $\eta \sim 1/T$ plot means a variation in the terms E_η and A of the equation $\eta = A\, e^{E_\eta/RT}$, with temper-:ature. In the case of water Eyring has explained this by postulating a change in the number of hydrogen bonds which have to be broken for flow to occur, i.e., the positive component of the entropy of activation shows a decrease with increase in temperature. Bernal(25) has shown that changes in configuration take place in water as the temperature alters and this will affect both the number and strength of the bonds present.

In the liquids considered here, in which a considerable degree of four fold coordination exists similar effects can be expected to be operative, i.e., the energy of activation varies as a result of changes in coordination and changes in the strength of the bonds. That this is so is indicated by the change in the thermo-:dynamic functions of viscous flow with temperature for these slags. This is shown for the slag 50% SiO_2 50% CaO. in graph 33.

Temperature °C.	$1/T$	E_η	ΔH	ΔG	ΔS
1614	5.3	36.7	33.0	37.6	-2.4
1467	5.75	40.2	36.7	37.8	-0.6
1380	6.05	47.1	43.8	38.2	3.4
1278	6.45	58.7	55.6	39.1	10.6


CaO-SiO2
50% SiO2 by Wt.
ΔS cals/degree
10
5
0
5
1200
1400
1600
ΔH K.cals/mol
60
50
40
30
1200
1400
1600
ΔG K.cals/mol
41
35
1200
1400
1600
Temp.°C

The energy of activation E_η was determined by drawing straight lines through the points over short ranges of temperature. All the slags examined showed a similar variation in the thermodynamic functions over this range of temperature, i.e., a large variation in ΔH and an increase in ΔG of approximately 2 k.cals. as the temperature decreased.

Due to thermal expansion a redistribution of electron density will take place as the interionic distance increases at higher temperatures. The strength of directed bonds will therefore decrease. In addition to this the structure is more open at higher temperatures, cations are less effectively screened and will tend to achieve higher coordination. The mean coordination of the system increases therefore at higher temperatures and thus causes a change in the free energy of activation. The large increase observed in the entropy of activation as the temperature falls is due to the increasing degree of structural bonding within the system. The presence of these directed bonds means that a large increase in the entropy of the ions occurs during the activated process of flow.

The free energy of activation is therefore a slowly varying function of temperature in these liquids and this is the same result as is obtained for water. Eyring stated that in liquids with structural bonding, such as water, while E_η showed a strong variation with

temperature, ΔG showed no such variation. However, Harrap and Heymann(23) pointed out that this was not quite correct and showed that in water ΔG did vary slowly with temperature just as in the liquids considered above. This is undoubtedly due to the changes in configuration as observed by Bernal(25).

Douglas(64) gave a more detailed model of the change in viscosity with temperature for silicate glasses. He consideres the units of flow to be the individual ions and successfully expresses the viscosity of a soda-silica glass by the equation

$$\eta/T = Ae^{A'/T} + Be^{B'/T}$$

The log $\eta/T \sim 1/T$ curve for this glass showed two linear portions with a curved intermediate part. The total viscosity is therefore composed of two parts. At high temperatures the contribution $Be^{B'/T}$ is insignificant and at low temperatures the contribution $Ae^{A'/T}$ is insignificant. At intermediate temperatures the two contributions are of comparable magnitude and hence the non-linear portion of the viscosity curve.

This equation may also be expressed

$$\eta/T = Ae^{A'/T}(1 + Ce^{C'/T})$$

and Douglas has equated $(1 + Ce^{C'/T}) = 1/w$ where w is the fraction of the total number of oxygen ions with two positions of minimum energy. Due to thermal expansion a point is reached when the oxygen ion between two silicon ions is unstable at the mid distance. It

is therefore offered two positions of minimum energy. The number of such oxygen ions changes with temperature and this Douglas considers to be the cause of the viscosity of such systems not obeying the simple relationship.

At low temperatures, due to the small value of w, the greatest contribution to the viscosity of the system is the energy required to provide room for the ions to move. The system then obeys the relationship $\eta/T = B e^{B'/T}$. At high temperatures, sufficient room is available and w is near unity; little energy is therefore expended in providing space. The system then obeys the relationship $\eta/T = A e^{A'/T}$. Application of this type of equation to the present results was not successful since the two increments A' and B', assuming these to be the only two operative, proved to be of comparable magnitude over the temperature range examined. It is worthy of note that the glass investigated by Douglas showed a slight variation in the log $\eta/T \sim 1/T$ plot for the high temperature portion which he has taken to be linear. His theory therefore is only a first approximation although it may be adequate to express the overall viscosity of a silicate system in the lower range of temperature,

i.e., the glassy range. When examined over higher ranges of temperature, however, as in these meta-:silicate liquids the process is seen to be more complex than can be accounted for by two simple energy increments.

P A R T 6.

SUMMARY AND REFERENCES.

SUMMARY.

1. A rotating cylinder viscometer has been designed and constructed for the measurement of the viscosity of liquid slag at various rates of shear up to a temperature of 1600°C. The viscometer has been calibrated by the empirical method using castor oil as a standard liquid and by the non empirical method utilising different lengths of inner cylinder. These two methods showed good agreement.

2. The viscosity of lime-silica, lime-magnesia-silica, and lime-manganous oxide-silica slags have been measured in the truly liquid and in the super-:cooled condition. Measurements at different rates of shear have given no evidence of a change in viscosity with change in rate of shear for any of the slags examined.

3. The viscosity ~ composition relationship in all the systems examined is smooth and continuous. No evidence has been obtained for the existence of a maximum or a minimum at compound compositions such as $CaO.SiO_2$ or $CaO.MgO.2SiO_2$. The $\log \eta$ ~ composition relationship for the metasilicate joins $CaO.SiO_2$ - $MgO.SiO_2$ and $CaO.SiO_2$ - $MnO.SiO_2$ is a smooth curve

with no inflections. In the lime silica system some indication has been obtained of a change in direction in the log $\eta \sim$ composition plot, at the metasilicate composition. The predominance of polymerised structure on the acid side of the system could lead to such an effect at the metasilicate composition.

It has been shown that the replacement of CaO by MgO at the $MO.SiO_2$ composition results in higher viscosity and the replacement of CaO by MnO in lower viscosity.

4. The energy of activation for viscous flow has been obtained for each slag composition from the plot log $\eta \sim {}^{1}/_{T}$. In the lime silica system the energy of activation increases with increase in silica content due mainly to the increasing structural effect of the Si - O bonding as the SiO_2 content increases and to the closer approach of cations in the increasingly polymerised melt.

The energy of activation for $MnO.SiO_2$ is less than for $CaO.SiO_2$ due to the higher ionic strength of the Mn^{2+} ion. The increased ionic strength from Ca^{2+} to Mn^{2+} reduces the structural effect of the Si - O bonding. An anomaly has been observed in the case

of $MgO.SiO_2$, the energy of activation being 30 k.cals/mol. This value is considerably greater than would have been expected for the Mg^{2+} ion of ionic strength 0.45 in six fold coordination. This anomaly is due to the entry of the Mg^{2+} ion into the fourfold coordinated arrangement like Si^{4+}.

It has also been shown that the viscosity of $MgO.SiO_2$ is greater than is consistent with this energy of activation of 39 k.cals/mol. This is due to the more complex flow process existing in the predominantly polymerised melt formed as a result of the Mg^{2+} ion entering into a state of low coordination.

The ratio E/W where E = Energy of Activation for viscous flow and W = Work of Cohesion has been calculated for each composition. The value of E/W is significantly greater than unity for the majority of the slags examined and this indicates the existence of associated complexes in the liquid slag. This is also taken as evidence that flow in these liquids is by movement of simple ions and not by the bulk movement of large silicate anions.

5. Consideration of the viscous properties of these metasilicate liquids in relation to other liquids indicates that their behaviour is intermediate between

the simple liquids (molecular liquids, simple ionic liquids) and the highly polymerised melts composed largely of SiO_2, P_2O_5, etc.

6. Qualitative observations on the extensive supercooling shown by these liquids indicates that supercooling is a minimum at compound compositions and a maximum at eutectic compositions. Compositions which separate silica on cooling, do not supercool.

The form of the log $\eta \sim 1/T$ relationship has been shown to be non linear for these supercooled liquids, i.e., the equation $\eta = A e^{E_\eta/RT}$ is not obeyed. This is due to the configuration of the liquid changing with temperature, resulting in a change in the number and in the strength of the bonds involved in the flow process.

7. The results obtained here for these metasilicate compositions have been shown to be in line with other fields of work for the same compositions, e.g., surface tension, electrical conductivity.

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APPENDIX.

TABLES OF VISCOSITY.

Lime-Silica.

48 Wt.% SiO_2		50 Wt.% SiO_2	
Temp. °C.	Poise.	Temp. °C.	Poise.
1603	1.68	1600	1.94
1581	1.86	1576	2.18
1553	2.15	1564	2.34
1532	2.44	1546	2.59
1506	2.82	1520	3.08
1485	3.21	1505	3.33
1466	3.62	1488	3.72
1441	4.35	1467	4.26
1421	4.99	1448	4.85
1401	5.85	1427	5.66
1371	7.56	1402	6.94
1348	9.28	1376	8.70
1323	11.75	1361	9.63
1304	14.38	1338	11.8
1275	20.15	1312	16.1
1253	25.6	1286	21.55
1217	41.6	1262	27.8
1183	68.5	1243	36.3
1152	123.0	1221	48.3
		1193	73.2

$CaO.SiO_2$.
51.7 Wt.% SiO_2.

Temp. °C.	Poise.
1605	2.17
1595	2.29
1587	2.36
1575	2.54
1556	2.82
1540	3.08
1528	3.30
1515	3.55
1501	3.90
1484	4.34
1464	4.97
1446	5.66
1427	6.52
1409	7.40
1396	8.25
1384	8.92
1367	10.51
1350	12.35

52.5 Wt.% SiO_2.

Temp. °C.	Poise.
1603	2.33
1586	2.59
1569	2.82
1551	3.22
1539	3.42
1520	3.80
1498	4.33
1482	4.79
1467	5.34
1442	6.39
1422	7.48
1402	8.80
1386	10.05
1363	12.20
1353	13.52
1331	16.90
1308	21.50
1295	25.30
1264	35.70
1240	48.90
1211	73.30
1191	99.00

53.5 Wt.% SiO_2.

Temp. °C.	Poise.
1613	2.50
1604	2.57
1592	2.75
1585	2.82
1573	3.04
1557	3.34
1544	3.63
1531	3.89
1522	4.10
1503	4.60
1494	4.90
1478	5.45
1465	5.99
1447	6.83
1428	7.88
1401	9.84
1391	10.75
1371	12.92
1358	14.50
1347	16.20
1325	20.70
1311	23.80
1297	28.40

54.5 Wt.% SiO_2.

Temp. °C.	Poise.
1620	2.67
1604	2.90
1600	2.94
1590	3.14
1585	3.21
1579	3.32
1571	3.50
1560	3.72
1554	3.85
1543	4.12
1531	4.49
1522	4.70
1510	5.06
1500	5.37
1480	6.23
1474	6.57
1462	7.05
1451	7.61
1438	8.40
1426	9.31

55.5 Wt.% SiO_2.

Temp.°C.	Poise.
1620	2.89
1600	3.17
1594	3.27
1576	3.61
1568	3.83
1553	4.20
1536	4.65
1521	5.06
1493	6.15
1482	6.49
1463	7.56
1439	9.10
1421	10.50
1395	12.90
1374	15.70
1355	18.90
1336	22.50
1313	29.50
1287	39.80
1267	50.40
1253	58.90
1224	91.30
1205	122.0

56 Wt. % SiO_2.

Temp.°C.	Poise.
1602	3.35
1591	3.49
1574	3.86
1561	4.19
1547	4.47
1519	5.38
1507	5.86
1484	6.81
1466	7.74
1450	8.58
1435	9.75
1409	12.10
1392	13.80
1375	16.12
1351	19.41
1330	25.31
1309	33.00
1288	42.10
1259	58.50

58 Wt. % SiO_2.

Temp. °C.	Poise.
1611	4.03
1593	4.24
1578	4.73
1563	5.20
1548	5.63
1536	6.06
1519	6.75
1501	7.60
1485	8.60
1471	9.28
1459	10.33
1443	11.80
1420	14.30
1400	16.70
1381	19.90
1358	24.70
1334	32.00
1312	40.80
1292	52.00
1271	65.90
1246	93.00

60 Wt.% SiO_2.

Temp. °C.	Poise.
1597	5.27
1555	7.10
1531	8.40
1511	9.55
1486	11.04
1463	12.90
1443	15.05
1412	19.55
1381	25.45
1352	34.70
1331	43.40
1301	61.20
1572	6.36
1470	12.42

62.5 Wt.% SiO_2.

Temp.°C.	Poise.
1600	7.15
1582	7.68
1574	7.93
1557	8.77
1545	9.57
1530	10.65
1518	11.58
1504	12.80
1483	14.90
1469	15.97
1457	18.20
1439	21.25
1427	23.60
1409	27.40
1391	32.00
1376	37.50
1345	52.60
1338	56.10
1320	70.20
1302	85.40
1281	119.30

65 Wt. % SiO_2.

Temp.°C.	Poise.
1596	10.31
1578	11.50
1558	13.18
1543	14.45
1523	16.72
1502	19.47
1484	22.25
1467	25.30
1453	29.25
1493	20.65

Lime-Magnesia-Silica. $CaO.SiO_2 - MgO.SiO_2$.

25 Wt.% $MgO.SiO_2$.

Temp.°C.	Poise.
1602	2.35
1561	2.90
1531	3.47
1492	4.40
1450	5.80
1417	7.35
1393	8.79
1360	11.38
1550	3.15
1412	7.65
1350	12.45
1304	19.40
1258	32.30
1233	43.75
1224	15.41
1271	26.90
1244	36.40

37.5 Wt.% $MgO.SiO_2$.

Temp.°C.	Poise.
1609	2.54
1592	2.75
1580	2.91
1556	3.30
1541	3.55
1524	3.95
1504	4.41
1483	4.94
1470	5.42
1441	6.66
1426	7.35
1409	8.35
1392	9.47
1374	11.10
1357	12.70
1341	14.65
1318	18.20
1304	20.75
1279	27.00
1262	32.70
1233	47.00

Lime-Magnesia-Silica.

$CaO.MgO.2SiO_2$.

46.3 Wt.% $MgO.SiO_2$

Temp. °C.	Poise.
1608	2.71
1587	3.00
1569	3.30
1545	3.70
1519	4.30
1503	4.72
1483	5.41
1448	6.96
1426	8.17
1409	9.40
1388	11.22
1370	13.15
1348	15.94
1326	19.73
1313	22.40
1288	29.70

57.5 Wt.% $MgO.SiO_2$.

Temp. °C	Poise.
1597	3.01
1577	3.31
1553	3.68
1537	4.11
1528	4.30
1508	4.83
1484	5.61
1462	6.45

75% Wt.% $MgO.SiO_2$

Temp.°C.	Poise.
1616	3.19
1603	3.38
1589	3.59
1582	3.78
1575	3.87
1561	4.21
1550	4.51
1534	4.92
1528	5.14
1509	5.84
1496	6.45
1485	6.91

85 Wt.% $MgO.SiO_2$.

Temp.°C.	Poise.
1626	3.36
1646	3.02
1602	3.67
1582	4.07
1557	4.82
1651	2.98
1592	3.82
1575	4.23
1552	4.91
1543	5.16

$MgO.SiO_2$.

Temp.°C.	Poise.
1610	4.12
1595	4.38
1578	4.71
1565	5.06
1582	4.63
1567	4.99
1557	5.30

Lime-Manganous Oxide-Silica. $CaO.SiO_2$-$MnO.SiO_2$.

20 Wt. % $MnO.SiO_2$

Temp. °C.	Poise.
1589	2.06
1567	2.29
1543	2.58
1528	2.78
1496	3.30
1472	3.77
1444	4.50
1414	5.55
1381	6.88
1346	9.06
1316	11.40
1294	14.23
1263	18.40
1238	24.00
1214	32.50
1186	44.60
1167	56.20
1140	86.60
1104	162.0
1066	333.0
1036	654.0
1010	1282

40 Wt. % $MnO.SiO_2$.

Temp. °C.	Poise.
1596	1.86
1568	2.10
1550	2.27
1530	2.50
1509	2.78
1488	3.09
1470	3.45
1447	3.94
1423	4.63
1401	5.37
1380	6.19
1358	7.17
1331	8.81
1318	9.70
1276	14.30
1250	18.65
1219	25.60
1178	41.60
1149	60.90
1108	113.0
1069	232.7

60 Wt.% $MnO.SiO_2$

Temp.°C.	Poise.
1600	1.63
1557	1.98
1535	2.18
1502	2.68
1478	3.03
1443	3.65
1408	4.54
1385	5.32
1342	7.17
1306	9.44
1288	10.80
1271	12.48
1239	16.71
1219	20.30
1196	25.40
1171	33.40
1141	49.00
1119	65.00
1096	94.50
1066	148.2
1042	236.5
1015	416.0
991	718.0
970	1345

80 Wt.% $MnO.SiO_2$

Temp.°C.	Poise.
1598	1.55
1576	1.70
1557	1.85
1541	1.96
1521	2.18
1503	2.36
1485	2.58
1470	2.78
1452	3.07
1431	3.47
1413	3.82
1400	4.15
1383	4.59
1354	5.60
1338	6.23
1316	7.20
1296	8.47
1273	10.00
1251	11.97
1240	13.17
1228	14.63
1211	17.00
1182	21.92
1157	27.96
1135	36.05
1119	44.20
1091	64.80
1066	96.30
1047	138.0
1018	260.0
995	538.0

$MnO.SiO_2$.

Temp.°C.	Poise.
1588	1.50
1562	1.59
1580	1.53
1550	1.67
1536	1.72
1566	1.56